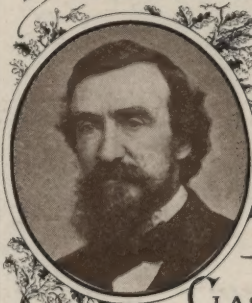


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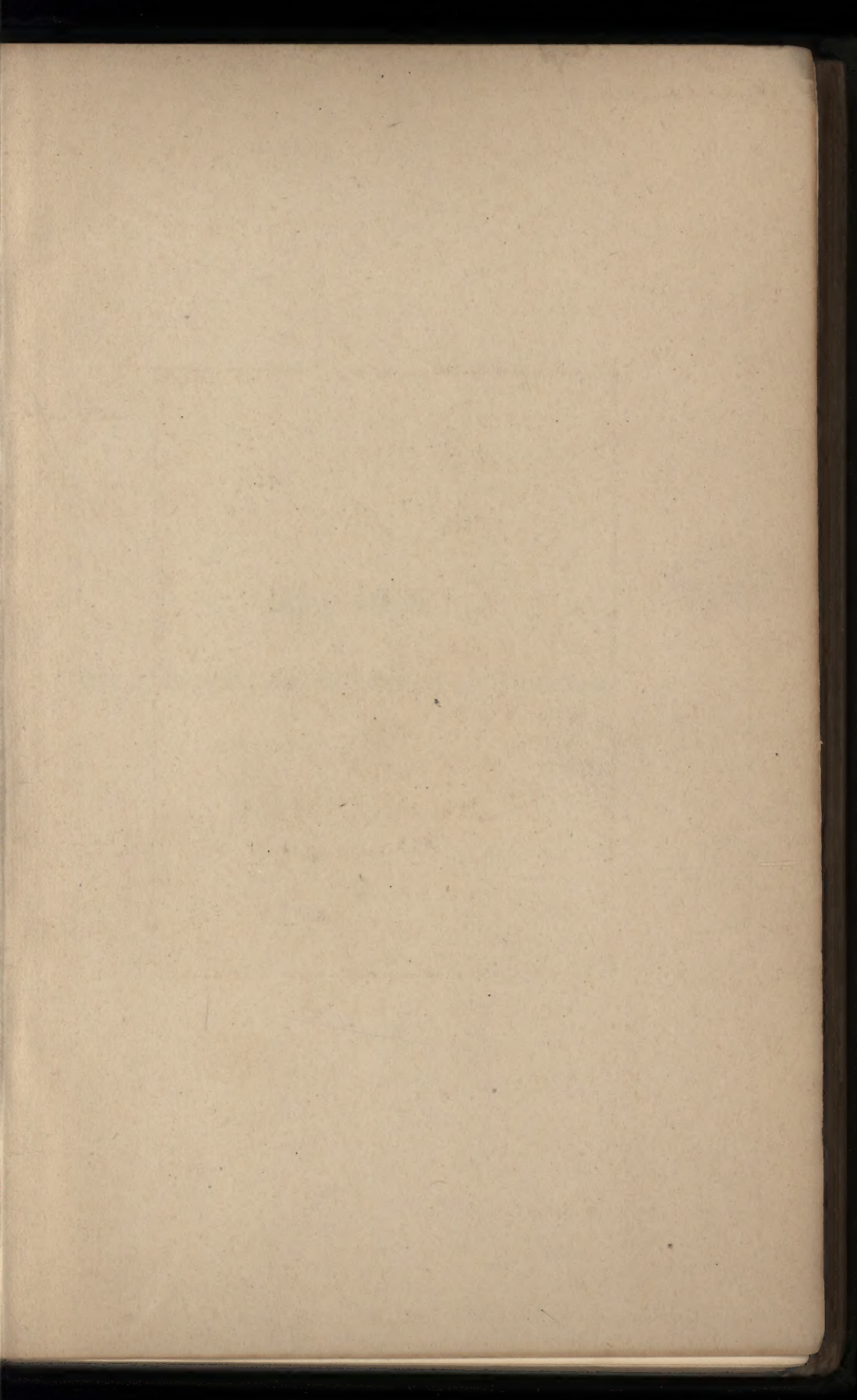
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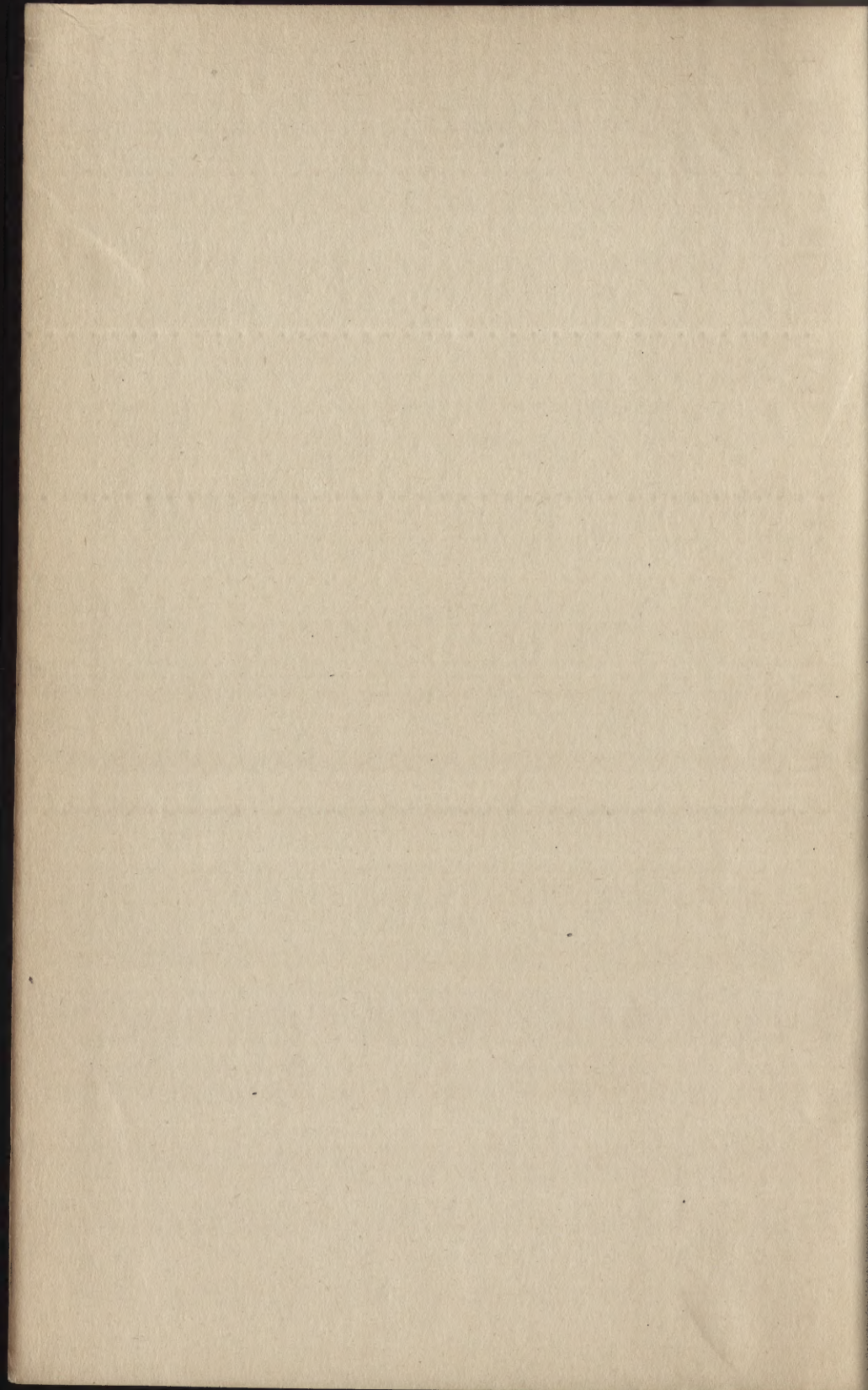
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JENA GLASS

AND

ITS SCIENTIFIC AND INDUSTRIAL APPLICATIONS





JENA GLASS  
AND  
ITS SCIENTIFIC AND INDUSTRIAL  
APPLICATIONS

BY  
DR. H. HOVESTADT

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FRANKLIN INSTITUTE  
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## AUTHOR'S PREFACE.

THIS book is mainly devoted to an account of the physical and chemical properties of the various types of glass which have up to the present been produced at the Jena Glass-making Laboratory, and to an indication of their scientific and industrial applications. The experimental and theoretical investigations relating to these glasses which are scattered through various journals, or have been published as separate monographs, are so numerous that a comprehensive summary of them has for some time been urgently needed.

When I undertook this task, I had no intention of limiting its scope to the Jena glasses. But the number of published investigations relating to other glasses admitting of definite identification is so small that, though they have received the same treatment, they form only an insignificant fraction of the whole.

If the plan of the book is somewhat out of the common, this is only in accordance with the special character of its subject.

H. HOVESTADT.

MÜNSTER, 1st Jan., 1900.

71058





## TRANSLATORS' PREFACE.

IN endeavouring to present Dr. Hovestadt's work in the clearest form to English readers, the translators have aimed at giving the spirit rather than the letter of the original. They have found it convenient, in many cases, to recast sentences and to supply missing steps in algebraic proofs. Brief explanations have occasionally been interpolated, and condensation has been employed in dealing with a few matters of very subordinate interest; due intimation being given of all material changes. Additions are indicated by square brackets or by the initials of one of the translators. In many cases the original memoirs have been consulted as a security against misapprehension. The abbreviated designations "Reichsanstalt," "Standards Commission," and "Bureau International" are substituted for the full titles "physikalisch-technische Reichsanstalt," "Normal-Aichungs-Kommission," and "Bureau International des Poids et Mesures."

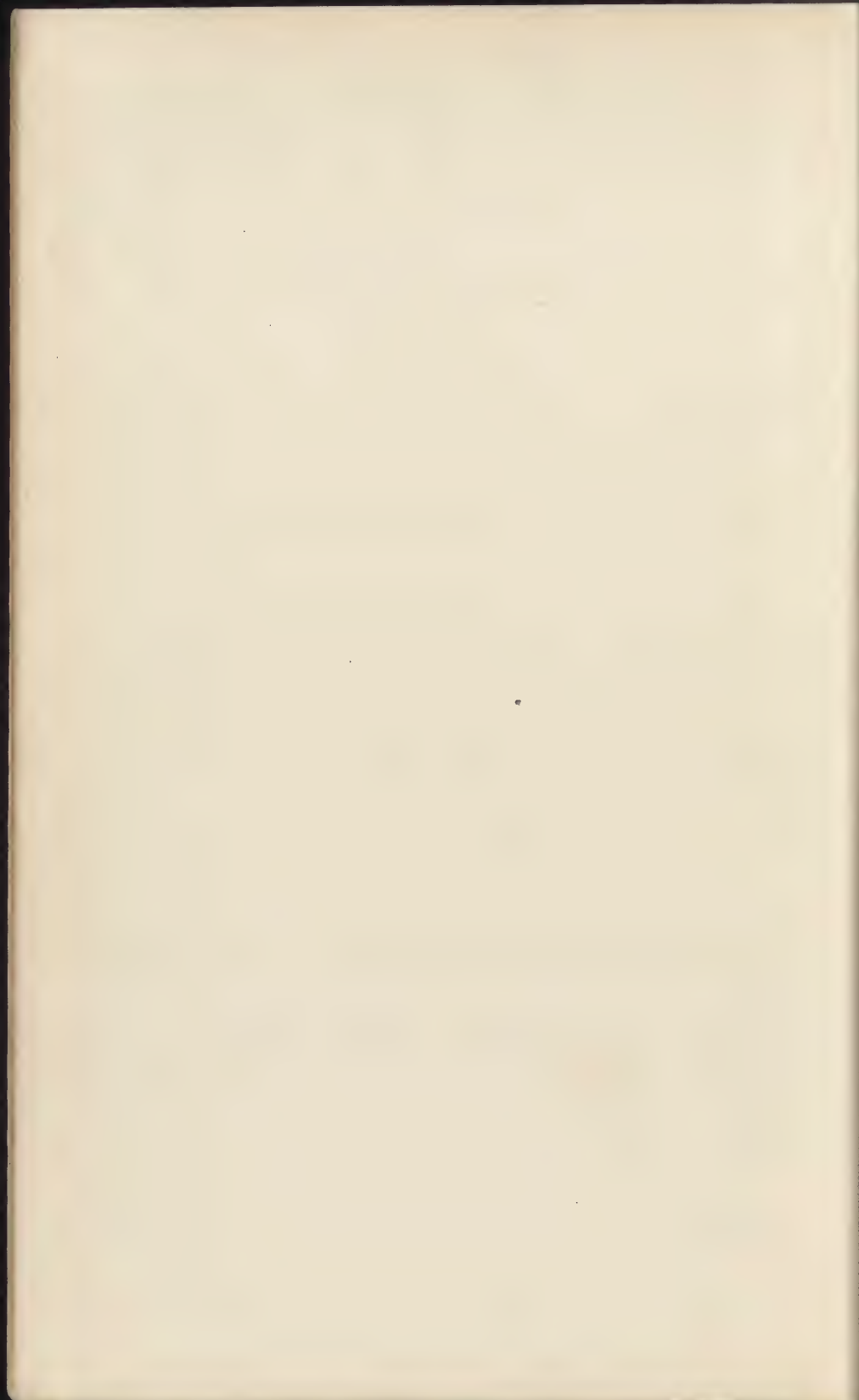
The Appendix includes a summary of more recent investigations, kindly furnished by Dr. Hovestadt for this edition; also the new Catalogue of Jena Optical Glasses issued in 1902, which introduces radical changes.

The Table of Contents is intended to give a clear idea of the scope and arrangement of the book. The Index will permit the quick finding of any desired item.

The translators desire to acknowledge their obligations to several friends for information and advice on various points; especially to Mr. H. J. Powell and Mr. W. Rosenhain, who have guided them in dealing with the technicalities of glass-making.

J. D. EVERETT.

A. EVERETT.





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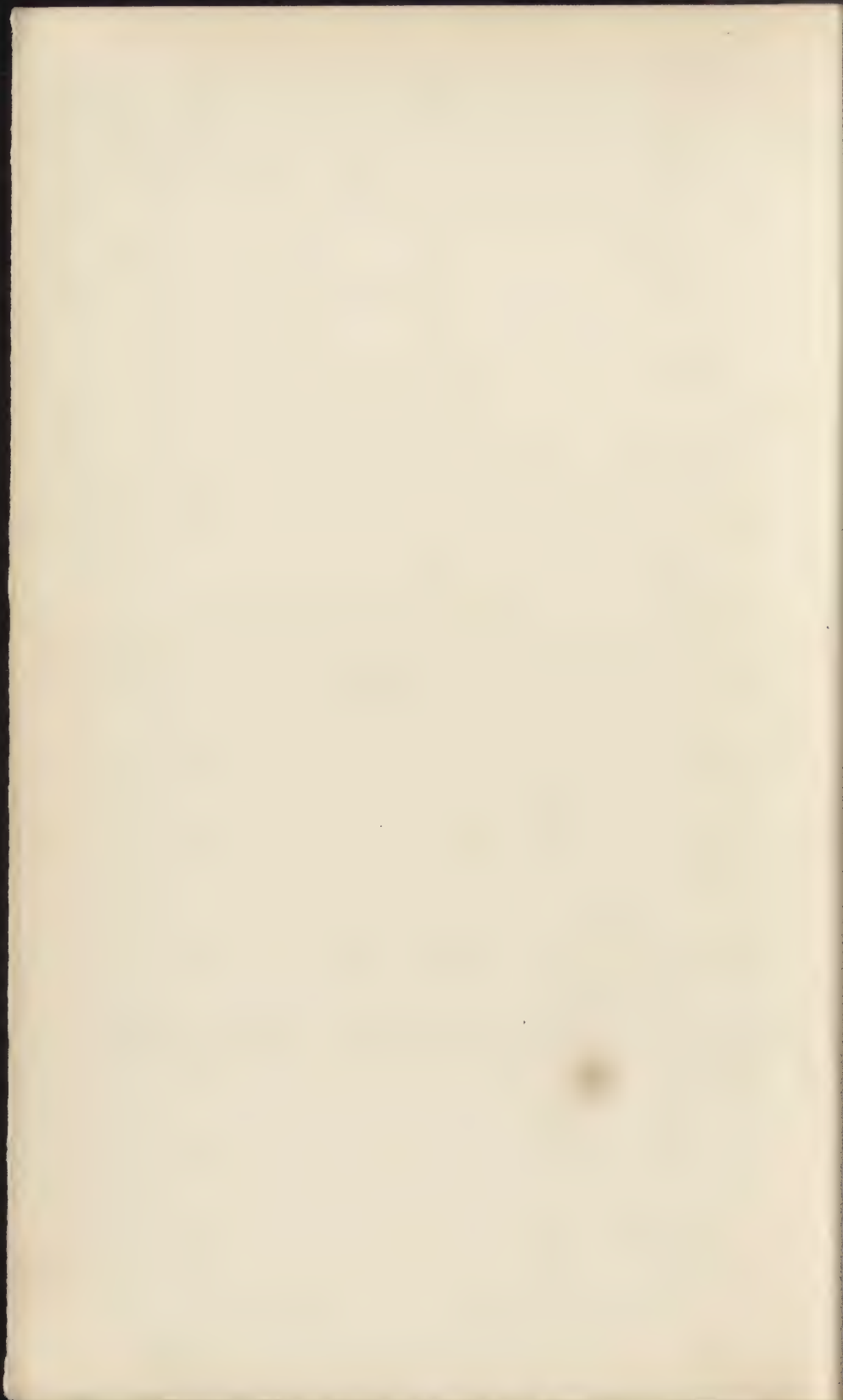
## ERRATA.

p. 44, line 15, read *fig. 2* (p. 41).p. 117, line 18, for *with a principal plane mirror*,  
read *each having a plane mirror*.

p. 157, line 17, for 0.2 mm., read 0.02 mm.

p. 188, lines 6, 7, 8, read *entered either the camera,*  
*or the observing telescope and apparatus for*  
*measuring  $\alpha$ .*p. 285, line 3 from bottom, for  $(100-q)^2$  read  
 $(100-T_q)^2$ .

JENA GLASS  
AND  
ITS SCIENTIFIC AND INDUSTRIAL APPLICATIONS





## CHAPTER I.

### INTRODUCTION.

1. The Jena glass-works originated in successful efforts to satisfy, by means of new glass fluxes, the increasing demands for excellence in refracting instruments. Newton<sup>1</sup> long ago asserted "that it is not the spherical figures of glasses, but the different refrangibility of the rays, which hinders the perfection of telescopes," and this is equally true of other optical instruments. Dollond, indeed, established the possibility (contrary to Newton's opinion) of combining two lenses into a doublet so as to bring pairs of colours to common foci on the axis, thus largely diminishing chromatic aberration. And Gauss showed that it was further possible, with the glasses known in his day, to render the resulting image almost entirely free from spherical aberration.

But the development of the art of glass-making in response to optical requirements kept, for a long time, to one narrow groove, and no new fluxes broke the monotony of a uniform series of crowns and flints. "Only<sup>2</sup> two earnest attempts were made to produce really new and optically improved glasses, one by Fraunhofer, the other by Harcourt, an English clergyman. With these two exceptions, all the efforts at improvement, and the great prizes offered by governments and corporations, were devoted to perfecting technical manipulation, and extending the series of dense flints—objects undoubtedly very important in themselves. Fraunhofer, besides taking, in conjunction with Guinand, a

<sup>1</sup> *Optics*, Prop. VII. (p. 4, vol. iv., Horsley).

<sup>2</sup> Czapski, *Zeitschr. f. Instrumentenk.* 6. 341 (1886).

prominent part in this extension, published the results of spectrometric determination for seven glasses, of which two, designated 'Flint No. 13' and 'Crown Lit. M,' showed decided diminution of the secondary spectrum. He appears, however, never to have attempted to produce these glasses except in small quantities; there is no record of their having gone through the melting pot in the way of ordinary manufacture, nor of discs for objectives being made of them. It may be that the difficulties in the way of producing them on a practical scale were found insuperable; or their mechanical properties may have rendered them unserviceable."

"Fraunhofer's experiment was thus practically fruitless, and Harcourt's attempts did not fare much better. Stokes, in *British Association Reports*, 1871 and 1874, has given an account of Harcourt's work,<sup>1</sup> from which we learn that from 1834, for a quarter of a century, he laboured perseveringly at his experiments, making in all 166 different meltings. In the main he seems to have been on the right track, though he made some mistakes. His failure seems to have been due to want of the necessary practical appliances. He did not succeed in producing, from his small-scale meltings, pieces of glass sufficiently homogeneous to enable accurate spectroscopic determinations to be made. The uncertainty of these determinations reacted in turn upon the experiments, by not giving sufficiently definite indications to work from. The ultimate product of his work consisted of two 'nearly flawless' 3-inch discs of 'titanium glass,' and two of borate glass. On attempting to make a triple objective from these, it was found necessary to reject one of the titanium discs and replace it by a disc of ordinary crown. The completed objective, though otherwise inferior to a good one of ordinary glass, still fully sufficed to prove the possibility of abolishing the secondary spectrum."

2. Some years after the publication of Stokes' reports on Harcourt's attempts, a paper by Abbe appeared, discussing in detail the increased requirements which must be satisfied if any real improvement in the performance of refracting instruments was to be obtained. Though he was speaking of the microscope,

<sup>1</sup>Czapski also refers to a report by Safarik on attempts to improve the telescope. *Vierteljahrsschr. d. astron. Ges.* 17. 13 (1882).

his remarks are almost equally applicable to other refracting instruments. He arrives at the following conclusion:<sup>1</sup>

“The future of the microscope as regards further improvement in its dioptric qualities seems to lie chiefly in the hands of the glassmaker. The especial desiderata are a distribution of colour dispersion more favourable to the removal of the secondary spectrum, and a greater variability in the relation between dispersion and mean index. There is now a definite basis for the hope that these conditions will sooner or later be satisfied, and the way thus be opened to radical improvement in the microscope and other optical instruments. The limitations observed in the connection between refraction and dispersion in existing glasses must not be regarded as a natural necessity; for among both natural minerals and artificial products, there are plenty of transparent substances which are known to have widely different properties as regards refraction and dispersion, though on other accounts they are scarcely available for optical purposes. Further, some experiments in the production of glasses with small secondary dispersion conducted by Stokes in England a few years ago, though barren of direct practical result, gave useful hints as to the specific effects of certain bases and acids on refraction of light. The uniformity shown by existing glasses in their optical qualities is probably chiefly due to the very limited number of materials hitherto used in their manufacture. Beyond silicic acid, alkali, lime, and lead, scarcely any substances have been tried, except perhaps alumina and thallium. When this narrow groove is left, and a methodical study, on an extended scale, is made of the optical qualities of chemical elements in combination, we may anticipate with some confidence a greater variety in the products.

“Unfortunately there seems little hope of material progress in this direction in the immediate future—a state of things very detrimental to the interests of science. The manufacture of optical glasses has for a long time been almost a monopoly; so few have been engaged in it that there could be no real competition. Since Daguet’s glass-works were given up, there have only been two establishments which supply public demands,

<sup>1</sup> “Die optischen Hilfsmittel der Mikroskopie,” *Bericht über d. wissenschaft. Appar. auf d. Londoner intern. Ausstellung i. J. 1876*, I. 417 (Brunswick, 1878).



for the third (the only one in Germany), founded by Utzschneider and Fraunhofer, is still in the exclusive service of one optical firm. It is true, as we are quite ready to acknowledge, that the art has in some respects made great advances even within the last few decades. Not only are the ordinary kinds of crown and flint produced with a perfection as regards clearness, homogeneity, and freedom from colour, never before attained, but the series of optical glasses has been greatly extended in one direction by the introduction of flint glasses which far surpass their predecessors both in refractive power and in dispersion. But these advances are confined to traditional lines. No inclination is shown to strike out a new departure, and endow practical optics with materials possessing new properties. In the absence of serious competition, it is not to the interest of the proprietors to try experiments with doubtful hope of profit. That an important industry, whose work is indispensable to many of the sciences, should be dependent upon a few individuals, is a highly undesirable state of affairs. It involves the danger (through some accident) of a complete stoppage of the whole supply, with disastrous results. It is therefore of vital importance, to all interests which are bound up with optics, that there should be more workers in the field, and that a spur to advance should be provided by increased competition.

"It is scarcely to be expected that private initiative, without strong backing, will supply the necessities of the case in time to prevent things from becoming much worse. The difficulties connected with such undertakings are so great, the initial outlay required is so heavy, and success, if attained, lies so far in the future, that there is little inducement to enterprise. A revolution of the industry can scarcely be brought about in any other way than by the means for its advancement being provided, in liberal measure, either by corporations or public authorities.

"This is a field in which learned societies, in a position to furnish material help for scientific requirements, could discharge a peculiarly useful and grateful office; for very important and diversified interests are dependent on the glass-making industry, its continued efficiency, and its further improvement. It is not microscopy alone that is here affected, but all sciences and arts that need optical appliances."

3. These remarks of Abbe's induced Schott, who, from personal study as well as from family tradition, was interested in glass-making, to take the work in hand. He accordingly communicated with Abbe, and they began in 1881 a joint investigation of the difficult problem. The results which ensued were narrated as regards their main features by the co-workers themselves, when, five years later, they placed their success at the disposal of the public. The preface to the first Trade Catalogue of the Jena Glass Laboratory, issued in July, 1886, runs as follows:

"The commercial undertaking hereby brought under public notice is the result of a scientific investigation into the dependence of the optical properties of amorphous combinations on their chemical composition, which was undertaken by the undersigned in order to bring to light the chemico-physical principles which underlie the manufacture of optical glass. This work was begun in January, 1881, and, in accordance with the plan laid down, Dr. Schott carried out the experimental meltings at Witten i. W., where he then resided; while the spectrometric examination of the specimens obtained was made in Jena by Professor Abbe, assisted by Dr. Riedel.

"The meltings at this stage were on a very small scale—not more than 20-60 gm.—and were solely directed to the purpose of studying, as accurately as possible, all chemical elements that could enter in any form into the composition of glasses, as regards their influence on refractive power and dispersion.

"In this way, towards the end of that year, a series of facts, as to the specific optical effects of certain substances, had been ascertained, which opened up prospects of obtaining new kinds of glass, better for some purposes than ordinary crowns and flints.

"In order to render these results as far as possible available for practical optics, it was resolved to adopt an enlarged programme, and, on the basis of the chemico-optical knowledge already acquired, systematically to form combinations of ingredients which, in their optical properties, most completely satisfy the optical desiderata, and at the same time fulfil the necessary practical conditions, as to hardness, durability, and freedom from colour. With this view, in the spring of 1882, Dr. Schott removed to Jena, where, in a building taken for the purpose, we set up a special laboratory provided with all the necessary apparatus. With the help of gas-furnaces and motor blowers, we were able

to make experimental meltings on the larger scale required, up to about 10 kgm.

"With the assistance of a young chemist for the analytical researches, which must necessarily go hand-in-hand with the synthetical work, and of a regular skilled operative, the experiments in this laboratory were continued to the end of 1883; mainly for the purpose of solving two independent problems arising from the requirements of practical optics.

"One was the problem of producing crown and flint pairs with as nearly as possible proportional dispersion throughout the different sections of the spectrum, in order to render possible a higher degree of achromatism than the glasses hitherto in use permitted, and thus abolish or diminish the strong secondary chromatic aberration which silicate glasses, by reason of the different distributions of dispersion in crown and flint, are never able to remove in achromatic combinations.

"The second problem, which we considered not less important than the first—though its importance has not hitherto been so generally recognised—was the attainment of greater diversity in the two chief constants of optical glass—mean index and mean dispersion.

"As a consequence of the uniformity of their chemical constitution, the silicate glasses hitherto in use could be arranged as a single series, in which, from the lightest crown to the densest flint (with some trifling exceptions) the dispersion steadily increased with the index.

"A theoretical discussion of optical problems places it beyond doubt that the construction of instruments to fulfil simultaneously several given conditions would be greatly facilitated, if the optician had at his disposal glasses of the same mean index and very various dispersions, and glasses of the same mean dispersion with very various indices. It is therefore an important step in advance, that the systematic use of a larger number of chemical elements in the composition of glass has rendered such gradations possible, and that, in several instances, the choice between available glasses, instead of being substantially of a linear character as heretofore, has become *two-dimensional*. The practical realisation of these advantages must be expected to take place gradually, being dependent on further progress in the theoretical calculation of optical constructions.



"To what extent our efforts in the two directions indicated have led to tangible results, may be seen from the accompanying catalogue of optical glasses, which have been made and can be reproduced to order.

"We propose hereafter to publish a connected account of the scientific results of these investigations, which contain the chemico-optical foundations for the production of the different kinds of glass. We will now only remark that these results were in the main established before the autumn of 1883, and that the whole investigation, as a scientific preparation for the rational manufacture of optical glass, would then have been brought to a conclusion, had we not received at this time, from several eminent scientists, the suggestion that we should ourselves take in hand the introduction of our results into practice, and follow up our laboratory work by undertaking the commercial production of optical glass.

"We accordingly, in conjunction with Drs. Carl and Roderich Zeiss, who had materially supported our labours from the very beginning, established a glass factory at Jena, with all the appliances for regular manufacture. By the autumn of 1884 we were in a position to commence the wholesale production of optical glass, both of the old and new varieties.

"We have to express our sincere thanks to the Prussian Bureau of Education and to the Diet of the Kingdom for the very liberal subsidies by which we were enabled to carry out the costly experiments on a manufacturing scale.

"After overcoming the many and great difficulties which environ a branch of technology hitherto untrodden, where every step has to be won by individual effort, this factory has now been in operation for nearly a year, and the experience which has been obtained in our dealings with most of the German optical factories enables us to enter confidently into public competition."

4. The optical business was then a rising one in Germany, and the immediate success of the new undertaking was due to the fact that it met a home want. Hitherto German opticians had been dependent upon import for their chief material.

Meanwhile other problems confronted the promoters. The annoyance caused by the deterioration to which thermometers of German make were subject, caused many appeals to be made to

the Jena works to take in hand the improvement of thermometer glass; and, after some hesitation, it was decided to do so. In March, 1883, Schott made his first trial-melting for the purpose, and by the autumn of 1884 the firm were able to place their first improved thermometer tubes upon the market, though experiments to test the thermometric properties of different meltings were continued for many years longer.

Under the circumstances, it will be readily understood that the intended publication of the results of the chemico-optical researches was long deferred, and indeed never carried out with the fulness originally intended. Schott, however, gave some of the main points in a paper read at Berlin in 1888.<sup>1</sup>

When Abbe and Schott began their experiments, there were only five glass-forming oxides whose optical effects were well known, viz.: silicic acid, potash, soda, lead-oxide, and lime. In the case of optical glasses, the necessary requirements placed difficulties in the way of introducing new elements.

The flux must not act upon the material of the crucible, and so absorb impurities.

Elements which evaporate during the process tend to produce veins, and should not be used.

Cloudiness, crystallisation, and bubbles, must be avoided in the operations of melting, cooling, and subsequent reheating to the verge of melting; this last being necessary for shaping irregular pieces to the desired form.

It must be possible to bring the glass from the plastic to the solid state without producing stress.

The glass must not be tarnishable; that is, must not be attacked by the moisture of the air.

The glass must be colourless; and lastly,—

It must be strong enough to bear the manipulation necessary in grinding and polishing.

5. Besides silicic acid, the only glass-making acid oxides known are boric acid, phosphoric acid, and perhaps arsenic acid. There was a tradition that they only gave tarnishable glasses; but as this seemed to require proof, the experimenters determined to start by testing the optical values of phosphoric and boric acid,

<sup>1</sup> "Ueber Glasschmelzerei für opt. und andere wissensch. Zwecke," *Verein zur Beförderung des Gewerbefleißes*, 4th June, 1888.

in combination with as many metallic oxides as possible. The meltings were made in tiny crucibles of only 20-30 c.c. capacity, with an ordinary laboratory gas-blast. But, though the mixture was kept thoroughly stirred, it was found impossible, in most cases, to obtain pieces of glass of sufficient size and homogeneity to admit of complete spectroscopic measurement.

The next step was to try somewhat larger quantities. At this stage Fletcher's gas furnace was found very useful. First, on a small scale, and driven by bellows, it gave lumps of glass weighing up to 150 g. Then, when it was enlarged, and fitted with a motor-blower, masses of 10 kg., and at a later stage, of 25 kg., were obtained with it. The melting pots were made of porcelain or fire-clay.

In addition to the six usual elements, silicon, potassium, sodium, lead, calcium, and oxygen, the following 28 new ones were introduced by degrees, in quantities of at least 10 per cent.: boron, phosphorus, lithium, magnesium, zinc, cadmium, barium, strontium, aluminium, beryllium, iron, manganese, cerium, didymium, erbium, silver, mercury, thallium, bismuth, antimony, arsenic, molybdenum, niobium, tungsten, tin, titanium, uranium, fluorine.

6. It was soon seen that, by the introduction of new elements, one desired object could be attained, namely, variation of the hitherto fixed relation between refraction and dispersion. But, on the other hand, very few of the elements afforded means of rendering the dispersions of crown and flint more similar, and so shortening the secondary spectrum.

*Boric acid* is peculiar in lengthening the red end of the spectrum relatively to the blue. *Fluorine*, *potassium*, and *sodium* have the opposite effect.

It is a characteristic of the old silicate glasses that flint glass has a higher index and larger dispersion than crown, and lengthens the blue more than the red.

Hence it was obviously desirable to introduce into flint glass as large a percentage as possible of boric acid. "In fact, boric acid has become the essential for all flint glasses intended for shortening the secondary spectrum." (See Appendix.)

The corresponding problem of lengthening the blue relatively to the red in crown glasses is not so easy. Sodium, one of the



three available elements, has only very slight influence. Potassium must only be used in moderate quantities, about 25-30 per cent., in a silicate glass, as it tends to make the glass tarnishable. It was also found, by repeated experiment, to cause an increase of total dispersion, an undesirable attribute in crown glass. "Probably Fraunhofer's lost 'Crown Lit. M.,' with an improved secondary spectrum, was laid aside on account of being tarnishable, and became gradually disintegrated by exposure to the air."<sup>1</sup>

Fluorine would be by far the most advantageous element to introduce; since, besides lengthening the blue end of the spectrum, as desired, it lessens the dispersion throughout the middle portion of the spectrum, which is a useful quality for the part played by a crown glass.

"A great number of experiments in this direction have shown us the possibility of producing colourless glasses, containing a large percentage of fluorine, in combination with lithium, barium, aluminium with phosphoric acid, and calcium. But crucibles of silicious material must not be used, as decomposition of the fluoride ensues, with generation of silicic-fluoride gas. For our experiments we used platinum crucibles and stirrers. But even with these, owing to the action of the oxygen and aqueous vapour present in the air, pungent fumes containing fluorine were given off, which were a perpetual source of variation in the homogeneity of the mass during the cooling process.

"Before finally renouncing the use of an element so pre-eminently valuable in its optical qualities, further experiments ought to be tried on a larger scale. The use of platinum vessels will necessarily make the attempts costly."

A remark must be added on the optical effect of phosphoric acid. On comparing a phosphate glass with a silicate of the same total dispersion, the run of dispersion is found to be nearly the same for both, but the phosphate has larger indices, and is, therefore, better adapted than the silicate for achromatising borate flint glasses.

Stokes and Harcourt duly recognised the effect of boric acid, but they attributed to titanous acid the effect which was really due to phosphoric acid, their titanium glass having always contained a

<sup>1</sup> Czapski supposes Fraunhofer's "Flint No. 13" to have been a borosilicate, likewise perishable. *Zeitschr. f. Instrumentenk.* 6. 358 (1886).

large proportion of phosphoric acid. This explains why a titanium-silicate glass made by Hopkinson, at Chance's works, disappointed expectation.<sup>1</sup>

7. The above information given by Schott as to the refractive properties of chemical elements in glass fluxes is restricted to a brief summary of positive results. But full particulars of his experiments on *one* metal—lithium—are given in a paper<sup>2</sup> on lithium glass, which he published while still at Witten in 1882. It gives an interesting glimpse into the progress of the work, and the fact that the result was in the main negative may serve to give some idea of the amount of labour involved in the undertaking.

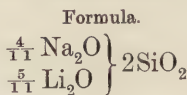
On melting down lithium carbonate with silicic acid, it was found that lithium silicate does not harden amorphously, like the silicates of potassium and sodium, but by crystallisation, like the silicates of most metals. Two trial glasses, obtained by the addition of boric acid in different proportions, proved too fragile to be of any use.

The next step was to try meltings containing only sodium, lithium, and silicic acid. From preliminary trials, to test the proper proportions of acid and base, a mixture according to the formula  $\text{RO} \cdot 2\text{SiO}_2$  was found to work best; any considerable increase of silicic acid raising the melting point so high that it was difficult to completely liquefy the mass, and impossible to refine it. Next, it was found that with equivalent proportions of lithium and sodium, there was no danger of devitrification; and the percentage of lithium was then considerably increased in order to give prominence to the action of the metal.

After many experimental meltings, the limiting conditions for obtaining clear glass were at last determined. A start was then made with the following working formula:

## I.

Recipe.		Calculated Composition of Resulting Glass.	
$\text{SiO}_2$	132.0 g.	$\text{SiO}_2$	78.10 %
$\text{Na}_2\text{CO}_3$	42.4	$\text{Na}_2\text{O}$	13.64
$\text{Li}_2\text{CO}_3$	37.0	$\text{Li}_2\text{O}$	18.26
	211.4 g.		

<sup>1</sup> Czapski, *ibid.* 359.<sup>2</sup> *Verhandl. d. Vereins z. Beförd. d. Gewerbeft.* 1882.

A spectroscopic examination by Abbe gave  $n=1.507$  for the index of the  $D$  line. This is only a little less than the index of ordinary silicate crown, and there was therefore nothing remarkable about the glass in this respect. A reliable determination of the dispersion was impossible owing to the numerous veins present.

Two other lithium glasses made by Schott had the following compositions:

## II.

Recipe.	Calculated Composition of Resulting Glass.	Formula.
$\text{SiO}_2$ 120.0 g.	$\text{SiO}_2$ 73.71 %	$\left. \begin{array}{l} \frac{4}{10} \text{Na}_2\text{O} \\ \frac{6}{10} \text{Li}_2\text{O} \end{array} \right\} 2\text{SiO}_2$
$\text{Na}_2\text{CO}_3$ 42.4	$\text{Na}_2\text{O}$ 15.23	
$\text{Li}_2\text{CO}_3$ 44.4	$\text{Li}_2\text{O}$ 11.06	
206.8 g.		

## III.

Recipe.	Calculated Composition of Resulting Glass.	Formula.
$\text{SiO}_2$ 240.0 g.	$\text{SiO}_2$ 73.04 %	$\left. \begin{array}{l} \frac{8}{20} \text{Na}_2\text{O} \\ \frac{13}{20} \text{Li}_2\text{O} \end{array} \right\} 2\text{SiO}_2$
$\text{Na}_2\text{CO}_3$ 85.0	$\text{Na}_2\text{O}$ 15.09	
$\text{Li}_2\text{CO}_3$ 100.0	$\text{Li}_2\text{O}$ 11.86	
425.0 g.		

Both these glasses had a somewhat greenish tint, but seemed otherwise clear and good. During melting, the mixture, while at white heat, was stirred four or five times, at intervals of 15 to 30 minutes, with a tube of unglazed clay, the quality of the glass being thereby much improved.

Information as to the optical results is contained in the following extract from a letter of Abbe's to Schott relating to preliminary testing:

"Though the material is still far from being entirely homogeneous, as you will see on inspecting the polished pieces, it is a great improvement on previous specimens. Among the fragments of No. III., I even found a prism from which I was able, with a little trouble, to get an accurate determination of the dispersion in various parts of the spectrum. I found for the absolute index of the  $D$  line

$$n_D = 1.5181,$$



and for the differences between the lines *B*, *D*, *E*, *F*, *G*:

$$\left. \begin{array}{l} n_D - n_B = 0.00358 \\ n_E - n_D = 0.00329 \end{array} \right\} n_E - n_B = 0.00687,$$

$$\left. \begin{array}{l} n_F - n_E = 0.00280 \\ n_G - n_F = 0.00513 \end{array} \right\} n_G - n_E = 0.00793.$$

The differences are reliable to 1 or 2 units of the last decimal place.

"As regards No. II., I have not yet been able to find a piece from which such a complete determination could be made. Hence I have only got for II. the index of the *D* line,

$$n_D = 1.5133,$$

and the dispersion for the interval *B* to *F*, which is approximately

$$n_F - n_B = 0.00962.$$

"I think we may therefore assume that the dispersions agree pretty closely with those of No. III.

"To give you an idea of the behaviour of your lithium glass as compared with the ordinary known glasses, I have tabulated, for several of them, my measures of the absolute index, and the dispersion, for the intervals *B* to *E*, and *E* to *G*, and also the ratio of the two partial dispersions for these intervals."

Abbe's table included, besides Schott's lithium crown, five crown glasses by Feil, Chance, and Daguet, and six flints by Feil and Chance. We will quote only the data for two of the Feil crowns and a Daguet magnesia crown.

	$n_D$	$n_E - n_B$	$n_G - n_E$	$k$
Crown ordinaire	1.514	0.00680	0.00792	1.165
" "	1.511	687	805	1.172
Lithium crown	1.518	687	793	1.154
Magnesia crown	1.517	753	898	1.193

The quantity  $k$  in the last column is the ratio of the dispersions in the two preceding columns.

"You will see from this that the lithium crown is much like ordinary crown glasses both in index and total dispersion. It only differs from them as regards the ratio of the dispersions for the two halves of the spectrum, which is 1.154 for the lithium as against 1.172 for the Feil glass preceding. Now, this difference

unfortunately lies in the wrong direction. For  $k$  being above 1.2 in all flint glass, and increasing rapidly with the dispersion, a crown glass will be the less fitted for an achromatic combination the smaller is the value of its  $k$ . Since it is just to the want of similarity in run of dispersions between crown and flint that secondary chromatic aberration is due, this aberration will be greater as  $k$  differs more for the two glasses used. It is therefore one of the most important problems in glass-making to produce either flint glass with small  $k$  and large enough total dispersion, or crown glass with large  $k$  and small enough total dispersion. The magnesia crown in the table, which for a long time has not been commercially obtainable, and since Daguet's death is no longer made, must therefore be regarded as the best crown glass hitherto manufactured for large telescope objectives.

"I regard it as a great achievement that you have succeeded in producing, from meltings in tiny crucibles, specimens good enough to admit of perfect optical investigation. Feil, though an eminent and experienced glass-maker, has never sent me any such which would allow of anything like an approximate estimate of the mean dispersion, much less a reliable determination of the partial dispersions. The most important condition for improvement in the manufacture of optical glass seems to me to be the practicability of making good (*i.e.* spectroscopically measurable) trial meltings, since in this way only is a course of methodical investigation possible. So long as one must make every trial with a quantity of 60 to 80 lbs. in order to get one small prism to examine, any systematic testing of new combinations will be out of the question. Hence, in spite of the negative result, I regard these researches as of more value than if they had led by a lucky chance to the discovery of a useful new glass."

8. To return to Schott's paper. He next goes on to describe experiments in connection with the subsidiary requirements mentioned above, which must be satisfied if a glass is to be practically serviceable as well as optically advantageous. This work, being necessarily of a purely empirical nature, was very tedious.

In phosphate and borate glasses, alkalis had to be used very sparingly, if at all, or tarnishing of the polished surface by dampness in the air was inevitable. However, by adding alumina,

zinc oxide, and barium oxide, the sensitiveness could be sufficiently overcome to render the resulting glasses serviceable. Many elements, it was found, could be advantageously replaced by others without change of optical effect. A number of elements had to be excluded on account of their colouring influence, and others from their rarity.

At last a series of phosphates, borates, and borosilicates were successfully produced in small quantities.

For thoroughly mixing the contents of the crucible, a porcelain agitator was used, which was rapidly revolved, and at the same time raised and lowered 5-10 cm. automatically. The crucibles were also of porcelain. But in spite of active stirring, it was found impossible to obtain large pieces free from veins.

In the hope of better success, it was decided to go to the cost of employing a platinum crucible of 3 litres capacity, with a platinum stirrer weighing  $1\frac{1}{2}$  kilogrammes. The result was an unpleasant surprise. Numerous bubbles appeared at the common surface of the glass and platinum; and the crucible disintegrated so rapidly that it only held out for four meltings. Later attempts with a smaller, very thick crucible, showed that platinum could be used for borates; but phosphates dissolve the metal and exude it again in gray masses during cooling.

9. It is very difficult, but at the same time indispensable—especially in making large objectives—to produce optical glasses free from stress acquired in solidification. The attention of the Jena makers was called to this difficulty by painful experience. A number of telescope objectives were ground by C. Bamberg, of Berlin, from discs of the new glasses, which had been cooled in the usual way and were apparently perfect. In spite of every care in workmanship, it was found impossible, when the telescopes were turned on stars, to obtain the well-known diffraction pattern of concentric circles; and the test by polarised light showed the presence of stresses, which were the cause of the failure.

This led to attempts at improved methods of annealing, which resulted in the adoption of the process designated "fine annealing." By means of a very large thermoregulator, which automatically controls the source of heat, the temperature can be kept steady for any length of time, at any point between  $350^{\circ}$  and  $477^{\circ}$ , or allowed to fall with any desired slowness. The glass is contained



in a very thick cylindrical copper vessel, on which a large gas flame plays. The temperature of the interior is measured, on the basis of Regnault's observations, by the pressure of mercury vapour, which is balanced by a column of mercury in an open tube; and the height of this column regulates the flame. By this fine-annealing method with the thermoregulator, even those glasses for which old methods had entirely failed were successfully freed from stress.

"The highest temperature to which we have ever found it necessary to raise a glass to make stress vanish, that is, to cause softening to begin,<sup>1</sup> was 465°. The lowest temperature ever required to ensure complete hardening was about 370°. Thus the temperatures of solidification all lie between 370° and 465°. We now spread this fall of 95° over an interval of four weeks, instead of a few days as formerly, with results far surpassing the best ever attained in the past."

At the time these words were written, a specimen of the fine-annealing process—an objective of  $6\frac{1}{2}$  in. aperture, with shortened secondary spectrum—had already been tried at Berlin Observatory, and proved its superiority to the older objectives.<sup>2</sup> It was shaped by Bamberg, who had not been disheartened by the previous failures, and whose unselfish devotion to the advancement of his art is warmly acknowledged by Schott.

10. The introduction of fine-annealing also enabled the Jena firm to practice a method of shaping lenses which had been tried at Paris many years before. The glass, while red hot, is pressed between metal cups having as nearly as possible the desired curvatures. If the ordinary annealing process be employed,

<sup>1</sup> The so-called softening point, *i.e.* the lowest permanent temperature at which a glass gradually loses the stresses caused in cooling, was determined by exposing a highly stressed short glass cylinder, with plane ends, to a fixed temperature for 20–24 hours, in the thermoregulator, and comparing the appearance in polarised light before and after the process. *Zeitschr. f. Instrumentenk.* xi. 330. 1891.

Pulfrich has since remarked that, in highly stressed glasses kept at constant temperature, measurable displacements, doubtless indicating partial loss of stress, are noticeable even at 100°, after an hour and a half. (See paper by Schott, *Ver. z. Beförd. d. Gewerbeft.*, Vortr. 1892, Apr. 4.)

<sup>2</sup> As further proofs of the success of the method, may be instanced the large discs for objectives afterwards made at Jena, which were  $1\frac{1}{2}$  metres in diameter, and weighed 7–9 cwt.

lenses of this sort are quite unfit for use in the better class of instruments. Their internal stress is sometimes so great that they fly in pieces as soon as grinding is begun. It is only by fine-annealing that they can be produced free from stress. The prevailing idea, that the pressure exerted on the glass while in a semi-liquid condition causes the internal stress, is, however, quite erroneous.<sup>1</sup> The production of pressed lenses has since been discontinued, as the method was unsuited for large objectives, and did not pay in the case of small ones. [For later information, see Appendix.]

11. In conclusion, Schott gives an account of the appliances and processes for the manufacture of ordinary optical silicate glasses, as employed at Jena in 1888.<sup>2</sup> The following is a sketch of the progress of a melting:

The melting pot, which must first be well dried, is very gradually raised in temperature for four or five days until it is red hot, when it is put in the melting furnace. Here it is further heated for five or six hours up to the melting temperature of glass, and then pieces of glass remaining over from former meltings (known in the trade as *cullet*) are put in. As soon as these are melted, the inside of the crucible is glazed with a great iron ladle. Then some of the glass mixture (technically called *batch*) is introduced, a little at a time, a fresh layer being added as soon as the previous layer is melted, till the crucible is full.

Then comes the second stage of the melting (called *plaining* or *fining*), the mixture being kept at a high temperature for six or eight hours as a rule. Great care and experience are required to maintain the right temperature during this period. If it is kept too low the bubbles are not removed; if it is raised too high the crucible is attacked, and clay is absorbed by the glass. At the conclusion of this stage, the firing is moderated for a time, the surface scum containing clay particles is removed, and a red-hot stirrer of fire-clay, in the form of a hollow cylinder 10-12 cm. in diameter, is placed in the glass and left for an hour to let the bubbles forming on it rise to the surface. Then begins

<sup>1</sup> "Influence of Cooling on the Optical Behaviour of Glass, and Production of well-annealed Pressed Lenses." *Communication from the Jena Glass Works*, Dec. 1889.

<sup>2</sup> Paper of 4 June, 1888, above quoted.

the process of stirring to produce complete incorporation, the handle of the stirrer being a long iron tube kept cool by a current of water. By blowing small flasks with a glass-blower's pipe it is seen when the glass is sufficiently clear; and the stirring is completed from three to four hours later, the mass in the meantime having been gradually cooling.

When the cooling is so far advanced that the stirrer can only be moved with difficulty, it is taken out, and the crucible, which with its contents weighs 15-20 cwt., is lifted out of the furnace, placed on a fire-brick platform, and left there to cool freely for half-an-hour or three-quarters.

It is then brought to the annealing furnace, in which the empty crucible to be used at the next melting has meanwhile been warming. Here, during the next three days, the mass cools completely down, generally flying into many pieces, large and small. These are carefully looked over, and faulty portions hammered off.

The remaining pieces are subjected to the moulding process (*Ramollieren*), by which the irregular lumps are made into rectangular or circular plates. To this end the glass is reheated in fire-brick moulds till it almost melts. A long tunnel-shaped oven is heated fully red hot at one end, while the other is just cool enough to admit of the moulds being pushed in.

The moulded glass is then put in the cooling kiln, where it is cooled in 10 or 12 days. This kiln is capable of containing 20-30 cwt. of glass in moulds.

When cool, the plates are polished on both sides so as to allow of clear vision through, and carefully examined for any remaining defects. If the plates fit for use amount to a fifth of the whole melting, the result is considered satisfactory.

12. The first price-list of the Jena Glass Works, issued in 1886, contains altogether 44 optical glasses, of which 19 are of essentially new composition. In the glasses of the silicate series, the index for crown could be vouched for to about 2 units of the third decimal place, for flint to about 3, and for very heavy flint to 6 or 8 units. To obtain greater exactness, special meltings were necessary in most cases.

In the case of several glasses, a caution is given that they "must be protected in use." This is explained as meaning that



though they are quite durable in ordinary air, there is danger in prolonged contact with damp in any form. Any deposit of moisture such as might be left by the touch of damp fingers, should be wiped off carefully before putting away.

Among glasses for special purposes are mentioned didymium-phosphate, cerium-phosphate, and uranium-phosphate.

The lively interest excited by the undertaking both at home and abroad was followed by a steady inflow of orders, which led to an enlargement of the list of glasses. In 1888 a Supplement was issued containing 24 additional glasses. Of these, 13 were new, including 8 baryta light flints, remarkable for smallness of dispersion compared to index, and intended chiefly for improving photographic objectives. So little lead oxide was required in their manufacture that the absorption usual in flints was reduced to quite a small amount.

Since, in the meantime, the composition of most of the crown glasses had been so improved as to render them almost perfectly colourless, objectives could now be constructed having greater transparency for the chemical rays than had previously been attainable.

Further, the extension of the choice of glasses gave means of correcting photographic objectives for astigmatism.

It was stated in the Supplement that the glasses O.197, S.35, S.17, S.10 were no longer regularly manufactured, on account of special difficulties attending their production, and of small demand.

In a second Supplement, issued in January, 1892, 8 more glasses, 6 of them new, were described, mainly intended for the same purposes as those of the first supplement. A caution was given respecting the two silicates, O.20 and O.13, of the first list, as being susceptible to damp. It was further stated that the crown glasses O.610, O.608, and O.381, formerly not quite satisfactory in this respect, had now been made more durable. The use of O.1209 in place of the baryta crown O.202 was recommended.

Most of the glasses which are important for the improvement of photographic objectives are extremely difficult to obtain free from small bubbles. The optical requirements leave too little room for the melter's choice, and it is impossible to produce large uniform masses not containing small isolated bubbles. The optical results in the camera are, however, practically unaffected, the

resulting loss of light, even in unfavourable cases, being barely  $\frac{1}{5000}$ th.<sup>1</sup>

13. The introduction of Jena glass into practical optics was initiated by Abbe, who was now enabled, with the help of the technical resources of Zeiss' optical works, to realise his long-cherished plans for the improvement of the microscope. A series of objectives and eye-pieces calculated by him were shown at the Naturforscher Versammlung in Berlin in 1886.

On the same occasion several astronomical objectives of 105-175 mm. aperture, made of Jena glass by Bamberg from Czapski's calculations, were also exhibited. Investigations with a view to perfecting astronomical objectives have been carried on at the Jena works until quite recently. Meanwhile, the practical application has been taken up by Zeiss, whose telescopic objectives and astronomical instruments were first advertised in 1899.

In the domain of photographic optics, the new glasses have given rise to a multitude of constructions.

14. On 2nd March, 1883, Schott made his first trial melting for thermometer glass. This was followed on 13th April by the melting designated No. IV., a pure lime-potash glass, and about 15th October by the melting No. VIII., a pure lime-soda glass.<sup>2</sup> Weber's observation, that pure potash glasses and pure soda glasses exhibit less thermal afterworking than those containing both alkalis, was fully confirmed. The further discovery that potash and soda produce equal amounts of afterworking was of considerable practical importance; for though it is easy to obtain soda free from potash, it is very difficult to obtain potash free from soda.

The introduction of new elements led to no immediate result, so far as the lessening of the total depression effect in the thermometer was concerned. One trial melting, 18<sup>III</sup>, a potash glass with a considerable percentage of boric acid and zinc oxide, was marked by the good agreement of a thermometer made of it with the air thermometer at medium temperatures. But the making and working of this glass presented difficulties.

It was sought to obtain the high power of endurance so essential for the best thermometer glass by using a large amount of lime

<sup>1</sup> *Mitteil. aus d. glastechn. Laborat. in Jena*, April, 1893.

<sup>2</sup> Schott's Paper of 4 June, 1888.

in combination with a moderate percentage of alumina. Trial meltings were made on a large scale with 16% of lime and 14% of soda. The resulting glass, though it certainly had small thermal afterworking, did not lend itself to manipulation with the blowing-pipe. It began to devitrify while the tube was being drawn out, unless it was kept at a high temperature during the process, which seemed scarcely possible. It also attacked the crucible, besides exhibiting a green tint difficult to get rid of.

These difficulties were overcome by employing additional ingredients. It was found, after a few experiments, that a composition containing 7% of zinc oxide, 7% lime, 14% soda, 2.5% alumina, and 2% boric acid, gave a good thermometer glass with great resisting power against all external influences. The addition of the 2% boric acid lowered the melting point without affecting the endurance.

With this glass, which was numbered 16<sup>III</sup> and designated *normal thermometer glass*, a definite advance was attained, and its permanent manufacture was commenced in 1885. It found a rival afterwards in the borosilicate 59<sup>III</sup>, and Schott has been constantly experimenting with a view to further improvements. It is scarcely necessary to remark that these researches are of purely scientific interest, having no commercial importance.

15. In the course of the thermometer glass investigations, it became important to know what causes contributed to facility of working.<sup>1</sup>

The glass made at the works in the Thuringian Forest stands repeated melting blowing and fusing without change; while ordinary glass, such as is used for windows, becomes rough and dull of surface, after even short exposure to the flame.

Enquiries elicited the information that Thuringian glass owed its special quality to a certain sand used in the making, which was only found in the neighbourhood of the village of Martinsroda. This had long been regarded as the one sand for the purpose, and all other quartz sands were believed unsuitable, especially the pure sand of Brandenburg.

Analysis of the Martinsroda sand showed that it contained 3.66 % of alumina, and it was natural to infer that this was the cause of its excellence. This inference was verified by analysis

<sup>1</sup> *Verhandl. des Ver. zur Beförd. d. Gewerbeft.* 1887, Dec. 4. Paper by Schott.



of Thuringian glass, and by experimental meltings in which pure quartz sand was used with and without the addition of alumina.

Schott suggests that the presence of the alumina hinders the volatilisation of the alkalis at the surface of the glass.

It is also possible that the dulling of the glass indicates incipient crystallisation, and that the alumina tends to prevent this.

16. As the Jena works have gradually developed, other new branches of manufacture have been taken up; the most notable being the production of glasses characterised by special powers of withstanding heat and chemical attack, which have rendered them very important both for scientific and commercial applications.

But, apart from these special problems, the establishment discharges important functions in the domain of pure science.

The long list of compositions employed by Schott—which already numbered over 1000 in 1886 and has since been continually increasing—shows how varied are the substances which we comprise under the name glass. The diversity in optical properties, which was the object originally sought, has brought with it an equally great diversity in all other physical and chemical properties. This opens up a rich field of investigation for which there was formerly little opportunity, owing to paucity of material for experiment.

Faithful to its original purpose, the Jena factory has carried on its work hand in hand with scientific research. The management has always shown readiness to assist the scientific investigations which have been undertaken in very various directions; and, by so doing, has obtained for itself the advantage of greater security against mere empirical working.

Though the results thus obtained are already considerable, a large number of questions still remain to be solved.

Attempts to establish a connection between the properties of glasses and their composition have hitherto been purely empirical. A more thorough treatment of this question must start with definite assumptions respecting the molecular constitution of glass—a subject at present obscure.

## CHAPTER II.

### OPTICAL PROPERTIES OF GLASS.

**17. Index and Dispersion.** For specifying the refractive properties of a glass, Abbe uses five bright spectral lines which can always be easily obtained from artificial sources, namely, the red potassium line, the yellow sodium line, and the lines  $H_\alpha$   $H_\beta$   $H_\gamma$  of hydrogen.<sup>1</sup> The second, third, and fourth are identical with the Fraunhofer lines  $C$   $D$   $F$  in the solar spectrum; the first lies near  $A$ , the fifth near  $G$ , and the five lines are denoted by the letters  $A'$   $C$   $D$   $F$   $G'$ . Their wave lengths are:

$A'$	$C$	$D$	$F$	$G'$
0.7677 $\mu$	0.6563 $\mu$	0.5893 $\mu$	0.4862 $\mu$	0.4341 $\mu$

$\mu$  denoting a micron or .001 mm. In the case of  $A'$  and  $D$ , which are double lines, the mean is taken.

For each glass five characteristic quantities are spectrometrically determined by Abbe's method,<sup>2</sup> in which a ray is made to retrace its path.<sup>3</sup> These quantities are: the index  $n_D$  for the

<sup>1</sup> Price list of the Jena glass-works for optical and other scientific purposes, third edition, p. 6.

<sup>2</sup> A short description of the method, with a literature list, is given by Pulfrich in Winkelmann's *Handbuch der Physik*, II. i. 307.

<sup>3</sup> Abbe's spectrometer, with which the observations are made, is described and figured at pp. 1-4 of Zeiss' *Catalogue of Spectrometers and Refractometers*, 2nd edition, 1899. The principle of the instrument is that, when the ray returns upon itself (the back of the prism being silvered) the angle of incidence on the prism is the same as for minimum deviation with a prism of double the angle.—J. D. E.

$D$  line; the mean dispersion  $\Delta$ , that is, the difference between the indices for  $C$  and  $F$ ; and the three partial dispersions,  $\delta_1$   $\delta_2$   $\delta_3$ , that is, the differences of index between  $A'$  and  $D$ , between  $D$  and  $F$ , and between  $F$  and  $G'$ . The accuracy of the measurements is sufficient for giving the index to four and the differences of index to five decimal places. As aids to comparison, four other quantities are deduced from these data, viz.:

$$\nu = \frac{n_D - 1}{\Delta}, \quad \alpha = \frac{\delta_1}{\Delta}, \quad \beta = \frac{\delta_2}{\Delta}, \quad \gamma = \frac{\delta_3}{\Delta}.$$

The first is the reciprocal of what is commonly called the "dispersive power," and may therefore be called the dispersive reciprocal, or the dispersive weakness; the last three may be called the partial dispersive ratios.<sup>1</sup>

The following list gives these characteristics, and also the density, for 76 typical Jena glasses, arranged in descending order of the values of  $\nu$ . Every glass has, besides the running number, a trade number with the letter O. or S. prefixed; O. (for Ordinary), signifying that the melting is performed in the ordinary way in a large crucible, and S. (for Special), that it is performed with special precautions in a small crucible. Glasses of essentially new composition are distinguished by heavy type.

The first part of the list, containing Nos. 1-44, was drawn up in 1886; and the accompanying explanation states that "for *ordinary* optical uses (opera-glasses, hand telescopes, small photographic instruments, telescopic and microscopic objectives not intended for very high-class work, small magnifiers, and eye-pieces of every sort) the crown glasses 5, 8, 13, 18, 23, and the flint glasses 29, 35, 36, 37, 38, 40 will suffice." The phosphates are recommended "where small dispersion and small dispersive power are desired"; combinations of phosphates and borates or borosilicates, "where, as in the better class of astronomical telescopes, the abolition or diminution of the secondary spectrum is important. In systems of lenses, such as microscopic objectives, which, for the best performance, require not only the closest agreement in run of dispersion between crown and flint, but also the best possible correction of spherical aberration and its

<sup>1</sup> The translators are alone responsible for these suggested designations. The original reads—"The first is the reciprocal of the relative mean dispersion; the three last may (in a somewhat different sense) be called relative partial dispersions."



chromatic difference, the theoretical or practical optician must exercise his judgment in making the best selection from the full list."<sup>1</sup>

The second portion of the list, containing numbers 45-68, was issued as a supplement in 1888. The new baryta flints here introduced are designed for photographic requirements. Numbers 69-76, which were contained in a second supplement issued in 1892, are mainly intended for the same purpose.

<sup>1</sup> Price List, 3rd edition, p. 17.

[A revised list of glasses, issued in 1902, will be found in the Appendix.]

Run- ning No.	Trade No.	Description.	Index for <i>D.</i>	Mean Dispersion <i>C</i> to <i>F.</i>	$\nu = \frac{n-1}{\Delta}$
1	O. 225	Light Phosphate Crown, - - -	1·5159	0·00737	70·0
2	S. 40	Medium Phosphate Crown, - - -	1·5590	0·00835	66·9
3	S. 30	Dense Barium Phosphate Crown, - -	1·5760	0·00884	65·2
4	S. 15	Densest Barium Phosphate Crown, -	1·5906	0·00922	64·1
5	O. 144	Boro-Silicate Crown, - - -	1·5100	0·00797	64·0
6	O. 57	Light Silicate Crown, - - -	1·5086	0·00823	61·8
7	O. 40	Silicate Crown, - - -	1·5166	0·00849	60·9
8	O. 60	Lime Silicate Crown, - - -	1·5179	0·00860	60·2
9	O. 138	Silicate Crown of High Index, - -	1·5258	0·00872	60·2
10	S. 52	Light Borate Crown, - - -	1·5047	0·00840	60·0
11	O. 20	Silicate Crown of Low Index, - -	1·5019	0·00842	59·6
12	O. 227	Barium Silicate Crown, - - -	1·5399	0·00909	59·4
13	O. 203	Ordinary Silicate Crown, - - -	1·5175	0·00877	59·0
14	O. 13	Potash Silicate Crown, - - -	1·5228	0·00901	58·0
15	O. 15	Zinc Silicate Crown, - - -	1·5308	0·00915	58·0
16	O. 211	Dense Barium Silicate Crown, - -	1·5726	0·00995	57·5
17	O. 153	Silicate Crown, - - -	1·5160	0·00904	57·2
18	O. 114	Soft Silicate Crown, - - -	1·5151	0·00910	56·6
19	O. 197	Boro-Silicate Glass, - - -	1·5250	0·00929	56·5
20	O. 202	Densest Barium Silicate Crown, - -	1·6040	0·01092	55·3
21	S. 35	Borate Flint, - - -	1·5503	0·00996	55·2
22	O. 252	Borate Flint, - - -	1·5521	0·01026	53·8
23	O. 152	Silicate Glass, - - -	1·5368	0·01049	51·2
24	S. 8	Borate Flint, - - -	1·5736	0·01129	50·8

Run- ning No.	Partial Dispersions, and ratios to $\Delta$ .			Density	Remarks.
	$\delta_1$ and $\alpha$ .	$\delta_2$ and $\beta$ .	$\delta_3$ and $\gamma$ .		
1	0·00485 0·658	0·00515 0·698	0·00407 0·552	2·58	Colourless.
2	0·00546 0·654	0·00587 0·702	0·00466 0·557	3·07	Do.
3	0·00570 0·644	0·00622 0·703	0·00500 0·565	3·35	Not very hard.
4	0·00591 0·641	0·00648 0·703	0·00521 0·565	3·66	Not hard ; needs protection.
5	0·00519 0·651	0·00559 0·701	0·00446 0·559	2·47	Exceptionally hard. Very colourless.
6	0·00530 0·644	0·00578 0·702	0·00464 0·564	2·46	
7	0·00545 0·642	0·00596 0·702	0·00479 0·564	2·49	
8	0·00553 0·643	0·00605 0·703	0·00487 0·566	2·49	Exactly corresponds to Chance's Hard Crown.
9	0·00560 0·642	0·00614 0·704	0·00494 0·567	2·53	
10	0·00560 0·667	0·00587 0·700	0·00466 0·555	2·24	Only to be used in protected places.
11	0·00543 0·645	0·00592 0·703	0·00478 0·568	2·47	
12	0·00582 0·640	0·00639 0·703	0·00514 0·566	2·73	Very colourless.
13	0·00563 0·642	0·00616 0·702	0·00499 0·568	2·54	
14	0·00572 0·635	0·00637 0·707	0·00515 0·572	2·53	Has better run of dispersion than ordinary silicate crown.
15	0·00587 0·642	0·00644 0·704	0·00520 0·568	2·74	
16	0·00630 0·633	0·00702 0·706	0·00568 0·571	3·21	Colourless.
17	0·00576 0·638	0·00637 0·705	0·00516 0·571	2·53	
18	0·00577 0·634	0·00642 0·705	0·00521 0·572	2·55	Corresponds to Chance's Soft Crown.
19	0·00599 0·645	0·00654 0·704	0·00531 0·572	2·64	
20	0·00690 0·632	0·00771 0·706	0·00626 0·573	3·58	Fragile. Cannot be freed from a few small bubbles.
21	0·00654 0·656	0·00699 0·702	0·00561 0·563	2·56	To be used in protected places.
22	0·00667 0·650	0·00722 0·703	0·00582 0·567	2·57	To be used in protected places.
23	0·00659 0·628	0·00743 0·708	0·00610 0·582	2·76	
24	0·00728 0·645	0·00795 0·704	0·00644 0·571	2·82	To be used under protection.



Run- ning No.	Trade No.	Description.	Index for <i>D.</i>	Mean Dispersion <i>C</i> to <i>F.</i>	$\nu = \frac{n-1}{\Delta}$
25	O. 164	Boro-Silicate Flint, - - - -	1.5503	0.01114	49.4
26	O. 214	Silicate Glass, - - - -	1.5366	0.01102	48.7
27	O. 161	Boro-Silicate Flint, - - - -	1.5676	0.01216	46.7
28	S. 7	Borate Flint, - - - -	1.6086	0.01375	44.3
29	O. 154	Light Silicate Flint, - - - -	1.5710	0.01327	43.0
30	O. 230	Silicate Flint of comparatively high index, - - - -	1.6014	0.01415	42.5
31	O. 184	Light Silicate Flint, - - - -	1.5900	0.01438	41.0
32	S. 17	Dense Borate Flint, - - - -	1.6467	0.01591	40.6
33	S. 10	Dense Borate Flint, - - - -	1.6797	0.01787	38.0
34	O. 118	Ordinary Silicate Flint, - - - -	1.6129	0.01660	36.9
35	O. 167	Ordinary Silicate Flint, - - - -	1.6169	0.01691	36.5
36	O. 103	Ordinary Silicate Flint, - - - -	1.6202	0.01709	36.2
37	O. 93	Ordinary Silicate Flint, - - - -	1.6245	0.01743	35.8
38	O. 102	Dense Silicate Flint, - - - -	1.6489	0.01919	33.8
39	O. 192	Dense Silicate Flint, - - - -	1.6734	0.02104	32.0
40	O. 41	Dense Silicate Flint, - - - -	1.7174	0.02434	29.5
41	O. 113	Dense Silicate Flint, - - - -	1.7371	0.02600	28.4
42	O. 165	Dense Silicate Flint, - - - -	1.7541	0.02743	27.5
43	O. 198	Very Dense Silicate Flint, - - - -	1.7782	0.02941	26.5
44	S. 57	Densest Silicate Flint, - - - -	1.9626	0.04882	19.7
45	O. 599	Boro-Silicate Crown, - - - -	1.5069	0.00813	62.3
46	O. 337	Silicate Crown, - - - -	1.5144	0.00847	60.7
47	O. 374	Silicate Crown, - - - -	1.5109	0.00844	60.5
48	O. 546	Zinc Crown, - - - -	1.5170	0.00859	60.2
49	O. 567	Silicate Crown, - - - -	1.5134	0.00859	59.7
50	O. 610	Crown of low index, - - - -	1.5063	0.00858	59.0

Running No.	Partial Dispersions, and ratios to $\Delta$ .			Density	Remarks.
	$\delta_1$ and $\alpha$ .	$\delta_2$ and $\beta$ .	$\delta_3$ and $\gamma$ .		
25	0·00710 0·637	0·00786 0·706	0·00644 0·578	2·81	
26	0·00690 0·626	0·00781 0·709	0·00644 0·584	2·73	
27	0·00762 0·627	0·00860 0·707	0·00709 0·583	2·97	
28	0·00864 0·628	0·00974 0·708	0·00802 0·583	3·17	To be used under protection.
29	0·00819 0·617	0·00943 0·710	0·00791 0·596	3·16	
30	0·00868 0·613	0·01009 0·713	0·00843 0·595	3·40	
31	0·00882 0·613	0·01022 0·711	0·00861 0·599	3·28	
32	0·00990 0·622	0·01123 0·709	0·00937 0·589	3·51	To be used under protection.
33	0·01097 0·614	0·01271 0·711	0·01062 0·594	3·81	To be used under protection.
34	0·01006 0·606	0·01184 0·713	0·01008 0·607	3·58	
35	0·01026 0·606	0·01206 0·713	0·01029 0·608	3·60	
36	0·01034 0·605	0·01220 0·714	0·01041 0·609	3·63	Exactly corresponds to Chance's Dense Flint.
37	0·01053 0·604	0·01243 0·713	0·01063 0·609	3·68	
38	0·01152 0·600	0·01372 0·715	0·01180 0·615	3·87	Optically identical with Chance's Extra Dense Flint.
39	0·01255 0·597	0·01507 0·717	0·01302 0·619	4·10	
40	0·01439 0·591	0·01749 0·718	0·01521 0·625	4·49	Corresponds to Chance's Double Extra Dense Flint.
41	0·01526 0·587	0·01870 0·719	0·01632 0·627	4·64	
42	0·01607 0·585	0·01974 0·720	0·01730 0·630	4·78	
43	0·01719 0·584	0·02120 0·721	0·01868 0·635	4·99	
44	0·02767 0·567	0·03547 0·726	0·03252 0·666	6·33	
45	0·00529 0·651	0·00569 0·701	0·00457 0·562	2·48	
46	0·00547 0·646	0·00596 0·704	0·00480 0·567	2·60	
47	0·00547 0·648	0·00593 0·703	0·00479 0·568	2·48	
48	0·00555 0·646	0·00605 0·704	0·00485 0·565	2·59	Almost absolutely colourless. Optical properties like English Hard Crown.
49	0·00554 0·645	0·00605 0·704	0·00488 0·569	2·51	
50	0·00552 0·643	0·00602 0·702	0·00489 0·570	2·51	Almost absolutely colourless.

Run- ning No.	Trade No.	Description.	Index for <i>D.</i>	Mean Dispersion <i>C</i> to <i>F.</i>	$\nu = \frac{n-1}{\Delta}$
51	O. 598	Silicate Crown, - - - - -	1.5152	0.00879	58.6
52	O. 512	Silicate Crown, - - - - -	1.5195	0.00886	58.6
53	O. 463	Baryta Light Flint, - - - - -	1.5646	0.01020	55.4
54	O. 608	Dispersive Crown, - - - - -	1.5149	0.00943	54.6
55	O. 602	Baryta Light Flint, - - - - -	1.5676	0.01072	53.0
56	O. 381	Dispersive Crown, - - - - -	1.5262	0.01026	51.3
57	O. 583	Baryta Light Flint, - - - - -	1.5688	0.01110	51.2
58	O. 543	Baryta Light Flint, - - - - -	1.5637	0.01115	50.6
59	O. 527	Baryta Light Flint, - - - - -	1.5718	0.01133	50.4
60	O. 575	Baryta Light Flint, - - - - -	1.5682	0.01151	49.3
61	O. 522	Baryta Light Flint, - - - - -	1.5554	0.01153	48.2
62	O. 578	Baryta Light Flint, - - - - -	1.5825	0.01255	46.4
63	O. 376	Ordinary Light Flint, - - - - -	1.5660	0.01319	42.9
64	O. 340	Ordinary Light Flint, - - - - -	1.5774	0.01396	41.4
65	O. 569	Ordinary Light Flint, - - - - -	1.5738	0.01385	41.4
66	O. 318	Ordinary Light Flint, - - - - -	1.6031	0.01575	38.3
67	O. 266	Ordinary Light Flint, - - - - -	1.6287	0.01775	35.4
68	O. 335	Dense Silicate Flint, - - - - -	1.6372	0.010831	34.8
69	O. 802	Boro-Silicate Crown, - - - - -	1.4967	0.00765	64.9
70	O. 709	Zinc Soda Crown, - - - - -	1.5128	0.00894	57.3
71	O. 1209	Densest Baryta Crown, - - - - -	1.6112	0.01068	57.2
72	O. 722	Baryta Light Flint, - - - - -	1.5797	0.01078	53.8
73	O. 846	Baryta Light Flint, - - - - -	1.5525	0.01042	53.0
74	O. 726	Extra Light Flint, - - - - -	1.5398	0.01142	47.3
75	O. 378	Extra Light Flint, - - - - -	1.5473	0.01193	45.9
76	O. 748	Baryta Flint, - - - - -	1.6235	0.01599	39.1



Run- ning No.	Partial Dispersions, and ratios to $\Delta$ .			Density	Remarks.
	$\delta_1$ and $\alpha$ .	$\delta_2$ and $\beta$ .	$\delta_3$ and $\gamma$ .		
51	0·00562 0·640	0·00619 0·704	0·00499 0·568	2·59	Almost absolutely colourless.
52	0·00568 0·641	0·00625 0·705	0·00504 0·568	2·64	Almost absolutely colourless.
53	0·00648 0·635	0·00720 0·706	0·00586 0·575	3·11	Almost absolutely colourless.
54	0·00595 0·631	0·00666 0·706	0·00543 0·576	2·60	
55	0·00675 0·630	0·00759 0·708	0·00618 0·576	3·12	
56	0·00644 0·629	0·00727 0·709	0·00596 0·582	2·70	
57	0·00696 0·627	0·00786 0·708	0·00644 0·580	3·16	
58	0·00699 0·627	0·00790 0·708	0·00650 0·583	3·11	
59	0·00706 0·623	0·00803 0·709	0·00660 0·582	3·19	
60	0·00718 0·623	0·00817 0·710	0·00672 0·584	3·15	
61	0·00718 0·623	0·00819 0·710	0·00677 0·587	3·03	
62	0·00777 0·619	0·00891 0·710	0·00739 0·589	3·29	
63	0·00814 0·617	0·00939 0·712	0·00787 0·597	3·12	
64	0·00857 0·614	0·00994 0·712	0·00837 0·600	3·21	
65	0·00853 0·616	0·00987 0·713	0·00831 0·600	3·22	Exactly corresponds to Chance's Light Flint.
66	0·00960 0·609	0·01124 0·714	0·00952 0·605	3·48	
67	0·01072 0·604	0·01270 0·715	0·01086 0·612	3·72	
68	0·01099 0·600	0·01308 0·714	0·01124 0·614	3·77	
69	0·00504 0·659	0·00534 0·698	0·00423 0·553	2·38	Not free from a few minute bubbles.
70	0·00575 0·642	0·00630 0·704	0·00508 0·569	2·58	
71	0·00680 0·636	0·00753 0·705	0·00610 0·571	3·55	Not quite free from a few minute bubbles.
72	0·00681 0·632	0·00761 0·707	0·00621 0·577	3·26	
73	0·00657 0·631	0·00736 0·707	0·00602 0·578	3·01	
74	0·00711 0·623	0·00810 0·709	0·00669 0·586	2·87	
75	0·00739 0·620	0·00847 0·710	0·00705 0·591	2·93	
76	0·00965 0·605	0·01142 0·713	0·00965 0·604	3·67	

**18. Achromatising one Glass by Another.** Let  $a', c, d, f, g'$  be the focal lengths of an achromatic doublet for the colours  $A', C, D, F, G'$ . We have

$$\phi = k(n-1) + k'(n'-1); \dots\dots\dots(1)$$

$\phi$  denoting the reciprocal of the focal length for any particular wave-length  $\lambda$ ;  $k$  the sum of the curvatures of the faces of the first lens (positive if convex);  $n$  its index for  $\lambda$ ; and  $k', n'$  the corresponding quantities for the second lens.

When  $\lambda$  is changed, (1) gives

$$\text{change of } \phi = k (\text{change of } n) + k' (\text{change of } n'). \dots\dots(2)$$

Using the notation

$$\begin{array}{ll} \Delta = n_F - n_C & \Delta' = n'_F - n'_C \\ \delta_1 = n_D - n_{A'} & \delta'_1 = n'_D - n'_{A'} \\ \delta_2 = n_F - n_D & \delta'_2 = n'_F - n'_D \\ \delta_3 = n_{G'} - n_F & \delta'_3 = n'_{G'} - n'_F, \end{array}$$

we have, as cases of (2),

$$\begin{array}{ll} \frac{1}{f} - \frac{1}{c} = k\Delta + k'\Delta' & \frac{1}{d} - \frac{1}{a'} = k\delta_1 + k'\delta'_1 \\ \frac{1}{f} - \frac{1}{d} = k\delta_2 + k'\delta'_2 & \frac{1}{g'} - \frac{1}{f} = k\delta_3 + k'\delta'_3. \end{array}$$

Let  $k$  and  $k'$  be so taken that  $f=c$ ; then

$$k\Delta + k'\Delta' = 0.$$

$$\text{Also } \frac{1}{d} = k(n_D - 1) + k'(n'_D - 1) = k\nu\Delta + k'\nu'\Delta' = k\Delta(\nu - \nu');$$

$$\text{whence } k = \frac{1}{d} \cdot \frac{1}{\Delta(\nu - \nu')}; \quad k' = \frac{1}{d} \cdot \frac{1}{\Delta'(\nu' - \nu)}. \dots\dots\dots(3)$$

$$\text{Hence } k\delta_1 = \frac{1}{d} \cdot \frac{\delta_1}{\Delta} \cdot \frac{1}{\nu - \nu'} = \frac{1}{d} \cdot \frac{a}{\nu - \nu'}, \quad k'\delta'_1 = \frac{1}{d} \cdot \frac{a'}{\nu' - \nu}.$$

$$\text{Thus } \frac{1}{d} - \frac{1}{a'} = \frac{1}{d} \cdot \frac{a - a'}{\nu - \nu'}, \quad \frac{1}{f} - \frac{1}{d} = \frac{1}{d} \cdot \frac{\beta - \beta'}{\nu - \nu'}, \quad \frac{1}{g'} - \frac{1}{f} = \frac{1}{d} \cdot \frac{\gamma - \gamma'}{\nu - \nu'};$$

whence

$$\left. \begin{array}{l} \frac{a - a'}{\nu - \nu'} = \frac{a' - d}{a'} = \frac{a' - d}{d} \quad \text{nearly,} \\ \frac{\beta - \beta'}{\nu - \nu'} = \frac{d - f}{f} = \frac{d - f}{d} \quad \text{"} \\ \frac{\gamma - \gamma'}{\nu - \nu'} = \frac{f - g'}{g'} \cdot \frac{d}{f} = \frac{f - g'}{d} \quad \text{"} \end{array} \right\} \dots\dots\dots(4)$$

the approximations being deduced from the consideration that the ratios of  $\alpha', d, f, g'$  to one another are sensibly unity.

Equations (4) give (in terms of the tabulated data for the glasses) the defect of achromatism for the colours  $A', D, G'$ , relative to  $C$  and  $F$ , which are united. The defects for the other colours can be deduced by interpolation, either graphical or arithmetical.

These equations show that two glasses will be the better fitted for achromatising, the less they differ as regards  $\alpha, \beta, \gamma$ , and the more they differ in  $\nu$ . Diminishing  $\alpha - \alpha', \beta - \beta', \gamma - \gamma'$  will, however, have no effect if  $\nu - \nu'$  diminishes in like measure at the same time. Further, from equations (3) we see that the curvatures of the lenses increase as  $\nu - \nu'$  diminishes. Perfect achromatising of one glass by another would, by equation (2), be attained if all the partial dispersions of the one were to those of the other in the fixed ratio  $\frac{-k'}{k}$ . The spectra of the two glasses would then be rigorously similar from a geometrical point of view. The differences exhibited by two glasses as regards the quantities  $\alpha, \beta, \gamma$  afford a measure of the dissimilarity of their spectra.

**19. Secondary and Tertiary Spectrum.** A clearer idea of the nature of this achromatising will be gained from a graphic representation. In fig. 1 the variation of focal length of a doublet with wave-length is shown for two combinations: (1) silicate crown 8 with silicate flint 36; (2) phosphate crown 3 with borate flint 24,—wave-length being taken as ordinate, and focal length as abscissa. Substituting the values of  $\alpha, \alpha', \nu, \nu'$ , etc., from the List, equations (4) give the following values for  $\alpha' - d$ , etc., in terms of  $d$  as unit (remembering that  $c = f$ ).

Combination.	$\alpha' - d$ .	$c - d$ .	$f - d$ .	$g' - d$ .
(1) 8 with 36, - -	+·00158	+·00046	+·00046	+·00225
(2) 3 with 24, - -	-·00007	+·00007	+·00007	+·00049

On inspecting the curves it will be seen that the scattering of foci is confined within much narrower limits in the combination (2) than in (1), and, further, that the colour union obtained is



triple instead of double. The parabolic curve (1) is cut by any ordinate in only two points, so that chromatic foci will only be united in pairs. But in curve (2), owing to the double bend, there will be union of *three* chromatic foci throughout the whole region extending from near  $A'$  to  $F$ , so that there only remains a slight scattering of the rays beyond  $F$ .

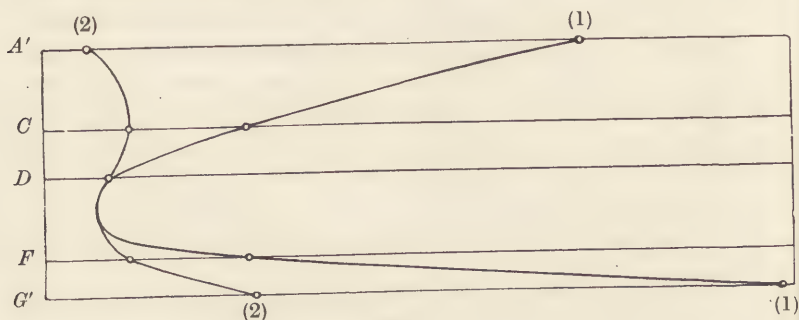


FIG. 1.

When the achromatism is such that the colours are only united in *pairs*, the residual spectrum is called *secondary*; when in *threes*, *tertiary*.

Thus combination (1) has a secondary spectrum of considerable extent, while (2) has only a tertiary spectrum, so short as to be relatively negligible.

These facts show what an improvement the new glasses have effected in achromatism. The glasses used in combination (1), an English hard crown and an English dense flint, are among the best of the old kind; and their secondary spectrum may be taken as representing about the best that can be done with silicate glasses. It is true that with heavy crown and light silicate flint doublets can be made in which the deviation from proportionality of dispersion is less; but this advantage is counterbalanced by diminution of the difference  $\nu - \nu'$ . For example, a combination of the glasses 17 and 31 gives a curve almost exactly coinciding with the curve (1) drawn above for glasses 8 and 36.<sup>1</sup> It was only with the introduction of phosphate and borate glasses that opticians were first enabled to form combinations which materially shortened the residual spectrum, and gave only a tertiary

<sup>1</sup> See "Mitteilungen aus dem glastechnischen Laboratorium, Jena," *Zeitschr. f. Instrumentenk.*, 6, 341 (1886) by Czapski, who points out the fruitlessness of such attempts.

remnant of colour. Besides 3 and 24, the pairs 3 and 28, 2 and 21, 1 and 21, 8 and 25 may be cited as examples.

**20. Another method of Achromatising.** The following way of treating the question was first proposed by Scheibner.<sup>1</sup> Let the lens-curvatures  $k$  and  $k'$  in equation (1) be so chosen that, for a particular colour defined by its wave-length  $\lambda_0$ , the focal length  $F$  of the doublet does not change for a small change of  $\lambda$ . This generally makes  $F$  a minimum. For visual purposes the selected colour should be in the brightest part of the spectrum—say,  $\lambda_0 = 55\mu$ ; for photographic work it should correspond to the place of strongest chemical action. Let  $n_0, n'_0$  be the two indices for  $\lambda_0$ ; then, putting  $\frac{1}{F_0}$  for  $\phi$  in equation (1), it becomes

$$\frac{1}{F_0} = k(n_0 - 1) + k'(n'_0 - 1),$$

and we are to have

$$0 = k \cdot dn_0 + k' \cdot dn'_0 \quad \text{or} \quad \frac{k'}{k} = -\frac{dn}{dn'};$$

whence

$$\frac{1}{kF_0} = n_0 - 1 - \frac{dn}{dn'}(n'_0 - 1),$$

$$\frac{1}{k'F_0} = n'_0 - 1 - \frac{dn'}{dn}(n_0 - 1).$$

From these two equations  $k$  and  $k'$  can be computed, if the ratio of  $dn/d\lambda$  to  $dn'/d\lambda$  is known. This ratio can be determined with sufficient exactness by employing an empirical dispersion-formula carried to three terms. If the formula is expressed in powers of  $1/\lambda^2$ , we may employ  $1/\lambda^2$  as the independent variable in the differentiations, instead of  $\lambda$ .

$k$  and  $k'$  having thus been found, equation (2) can be employed for computing the successive changes of  $1/F$ , starting from  $F_0$  and giving successive increments to  $\lambda$ . This will show the departure from achromatism in the various parts of the spectrum.

Czapski<sup>2</sup> has carried out this calculation for the three pairs

<sup>1</sup> Abhandl. d. Sächs. Akad. II, S. 565 (1876).

<sup>2</sup> Zeitschr. f. Instrumentenk., 6, 342 (1886). The numerical results and the three curves derived from them are also given in Winkelmann's *Handbuch d. Physik*, II. 1, pp. 146, 147.

8/36, 3/28, 3/24, starting from  $\lambda_0 = 0.55\mu$ , and proceeding, by increments  $\pm 0.04\mu$ , to  $\lambda = 0.77\mu$  in one direction, and  $\lambda = 0.41\mu$  in the other. The result is very similar to that obtained by uniting  $C$  and  $F$ .

The combinations 8/36 and 3/28 give parabolic curves, that is to say, secondary spectra, the second having about half the extent of the first; while, in the combination 3/24, the colour-union is so close that there is no material difference of focal length anywhere between  $A'$  and  $F$ .

**21. Diversity of Glasses.** If, taking  $n$  the index for  $D$  as abscissa, and the "mean dispersion"  $\Delta$  as ordinate, we plot on cross-ruled paper all the glasses given in Art. 17, it will be found that the old glasses, except a very few of small index, group themselves along a straight line, whose equation is approximately

$$\Delta = 0.07812n - 0.10962.$$

In virtue of this relation,  $\nu$ , which is defined as  $(n-1)/\Delta$ , is practically a function of only one independent variable instead of two. This limitation is largely removed by the new glasses, which, when introduced into the diagram, spread themselves over a considerable area, lying between the above-mentioned line and the axis of abscissae.<sup>1</sup>

The limitation just mentioned as holding for the older glasses implies that those which have equal  $\nu$ 's have also equal dispersions, and *vice versa*, so that large change of  $\Delta$  entails correspondingly large change of  $\nu$ . On consulting the catalogue (which is arranged in order of  $\nu$ ), another inconvenient uniformity in the older glasses will be found, namely, that similarity in *run* of dispersion accompanies equality in  $\nu$ . Here again the new glasses come to the rescue. Thus, comparing the old glasses 6, 7, 8, 9, with the new borate crown 10, we see that, while the values of  $\alpha$ ,  $\beta$ ,  $\gamma$  are almost the same for the four former; in 10 the red end of the spectrum is considerably lengthened, and the blue end shortened. Pairs 23/24 and 28/29 offer further illustrations

<sup>1</sup> For the first 44 glasses Czapski has plotted a diagram in *Zeitschr. f. Instrumentenk.*, 6, 345 (1886).



of the fact that, with the help of the new glasses, it is possible, without appreciably changing  $\nu$ , to give the different portions of the spectrum relatively unequal extents.

**22. Hypochromatic and Hyperchromatic Doublets.** The fact that the catalogue includes pairs of glasses exhibiting unequal dispersion for equal or nearly equal index, affords the possibility of a mode of combination which exaggerates the natural diversity of the glasses.<sup>1</sup>

Equation (1) of Art. 18, applied to a doublet composed of two lenses  $L$  and  $L'$  cemented together becomes, when  $n$  and  $n'$  are equal,

$$\frac{1}{F} = k_e(n-1), \dots \dots \dots (1)$$

$k_e$  denoting  $k+k'$ , that is, the sum of the external curvatures. We may call  $k_e$  the *total curvature* of the doublet.

Let  $\rho$  denote the resultant dispersion, defined, in accordance with equation (2) of Art. 18, by

$$k\delta + k'\delta' = (k+k')\rho = k_e\rho. \dots \dots \dots (2)$$

Then the doublet will be equivalent to a single lens of total curvature  $k_e$ , index  $n$ , and dispersion  $\rho$ .

The dispersion  $\rho$  can, if desired, be made either less than the less, or greater than the greater, of the two quantities  $\delta$ ,  $\delta'$ . In the first case the compound lens is called *hypochromatic*; in the second, *hyperchromatic*.

Equation (2) may be written in either of the forms:

$$\rho = \delta + \frac{k'}{k_e}(\delta' - \delta), \dots \dots \dots (3)$$

$$\rho = \delta' + \frac{k}{k_e}(\delta - \delta'). \dots \dots \dots (4)$$

Now  $k$  and  $k'$  are always of opposite sign. We shall assume

$k$  always positive, and  $k'$  negative.

<sup>1</sup> Cf. German patents Nos. 88889 and 92313, Zeiss.

Then we have the following results :

FROM EQUATION (3).	FROM EQUATION (3).
<p>If <math>k_e +</math> and <math>\delta' &gt; \delta</math>, then <math>\delta &gt; \rho</math>.</p>	<p><math>k_e +</math> <math>\delta &gt; \delta'</math> <math>\rho &gt; \delta</math>.</p>
FROM EQUATION (4).	FROM EQUATION (4).
<p>If <math>k_e -</math> and <math>\delta &gt; \delta'</math>, then <math>\delta' &gt; \rho</math>. (Hypochromasy).</p>	<p><math>k_e -</math> <math>\delta' &gt; \delta</math> <math>\rho &gt; \delta'</math>. (Hyperchromasy).</p>

Thus the limits of dispersion to which we are confined in dealing with a single glass of given index, may be enlarged by making use of a combination of two glasses which have this index. The lower limit may be lowered by giving the weaker dispersion to the positive component of a positive doublet, or to the negative component of a negative doublet. The upper limit may be raised by giving the stronger dispersion to the positive component of a positive doublet, or to the negative component of a negative doublet.

**Chromatic Difference of Spherical Aberration.** The condition  $n = n'$ , even if strictly fulfilled, can only hold for rays of one definite wave-length  $\lambda_0$ . Since these rays undergo no deviation at the common surface of contact, their spherical aberration is independent of the curvature of this surface, and is the same as for a simple lens of index  $n$  and curvature  $k_e$ .

The spherical aberrations of rays of other wave-lengths, though affected by the curvature of the internal surface, depend mainly upon the two external surfaces, and the same rule must hold for differences of spherical aberration resulting from difference of wave-length. Now, at the external surfaces, it is not the resultant dispersion  $\rho$ , but the individual dispersions  $\delta$  and  $\delta'$ , which actually come into play; and therefore, in the spectrum formed by the chromatic foci of the marginal zone, any colour whose wave-length is different from  $\lambda_0$  will have a somewhat different situation from what it would have in the case of a simple lens giving dispersion  $\rho$ . Thus, as regards chromatic differences of

spherical aberration, the compound lens is not exactly equivalent to the simple one. In the hypochromatic doublet the divergences will be somewhat greater, and in the hyperchromatic somewhat less than for the simple lens.

**23. Infra-red and Ultra-violet Spectrum.** An investigation of dispersion beyond the limits of the visible spectrum has been carried out by Rubens<sup>1</sup> and Simon<sup>2</sup> for 13 Jena glasses. As these glasses are not included in the List of Art. 17, they are tabulated here. Besides the ordinary data, the limits of wave-length to which the investigation extended in each case are given.

				10 <sup>5</sup> δ <sub>1</sub>	10 <sup>5</sup> δ <sub>2</sub>	10 <sup>5</sup> δ <sub>3</sub>
	<i>n<sub>D</sub></i>	10 <sup>5</sup> Δ	<i>ν</i>	10 <sup>3</sup> α	10 <sup>3</sup> β	10 <sup>3</sup> γ
S. 179. Medium Phosphate Crown, 2·020 μ—0·3261 μ,	1·56207	837	67·2	556 664	587 701	479 572
O. 1092. Light Baryta Crown, 2·200 μ—0·2763 μ,	1·51698	853	60·6	555 651	601 705	489 573
S. 204. Borate Crown, 1·977 μ—0·2763 μ,	1·51007	868	58·8	581 669	603 695	482 555
O. 1143. Dense Barium Silicate Crown, 2·113 μ—0·2837 μ,	1·57422	1006	57·1	640 636	704 700	584 581
O. 1151. Silicate Crown of high dispersion, 2·120 μ—0·2980 μ,	1·52002	1003	51·8	634 632	713 711	597 595
O. 451. Light Silicate Flint, 2·490 μ—0·2980 μ,	1·57524	1396	41·1	855 612	991 710	840 602
O. 469. Dense Silicate Flint, 2·502 μ—0·3261 μ,	1·64985	1927	33·7	1165 605	1382 717	1194 620
O. 500. Dense Silicate Flint; yellowish, 2·316 μ—0·3403 μ,	1·75130	2723	27·6	1600 588	1961 720	1709 628
S. 163. Densest Silicate Flint, yellow, 2·368 μ—0·4340 μ,	1·88995	3997	22·3	2293 574	2895 724	2603 651
O. 1442. Very dense Baryta Crown, 0·768 μ—0·3133 μ,	1·60956	1062	57·4	679 639	750 706	614 578
O. 1230. Dense Baryta Crown, 0·768 μ—0·2837 μ,	1·57363	1006	57·0	632 628	716 712	572 569
O. 1250. Crown of high dispersion, 0·768 μ—0·2980 μ,	1·52046	1010	51·5	636 630	706 699	589 583
O. 1398. Baryta Lead Glass, containing Alkali, 0·768 μ—0·3081 μ,	1·58282	1244	46·8	774 622	896 720	742 596

<sup>1</sup> Ueber Dispersion ultraroter Strahlen, *Ann. d. Phys. u. Chem.*, 45, 238 (1892).

<sup>2</sup> Ueber Dispersion ultravioletter Strahlen, *Dissert. Berlin*, 1894; Extract in *Ann. d. Phys. u. Chem.*, 53, 542 (1894).



**Infra-red Spectrum.**—Rubens determined the dispersion for the first nine glasses<sup>1</sup> from the  $G'$  line down to the limit mentioned, using the method of minimum deviation by prisms; with a bolometer for the infra-red region; the bolometer having an iron or platinum wire according as the dispersion was strong or weak.

A parallel beam of light, formed by placing a lens in the path of rays from a Linnemann's zircon burner, was thrown at  $45^\circ$  upon a pair of glass plates pressed together so that the layer of air between was very thin. The reflected rays were brought, by a second lens, to a focus on the slit of a spectrometer, the image of the source filling the entire length of the slit. In the spectrum formed by the instrument dark vertical bands were seen, due to interference of rays reflected at the two surfaces bounding the thin layer of air. The wave-lengths of the extinguished rays are determined from the equation,

$$m \cdot \lambda_m = K, \dots\dots\dots(1)$$

where  $m$  is any one of a series of consecutive integers, and  $K$  a constant equal to  $2d \cos \alpha$ ,  $d$  denoting the thickness of the layer of air, and  $\alpha$  the angle of incidence on the glass, here  $45^\circ$ .

The deviations for the four lines of known wave-length,  $G'$ ,  $F$ ,  $D$ , and  $C$ , were determined from the scale-readings; and the wave-length corresponding to any other deviation could then be obtained by graphic interpolation. The wave-lengths for the interference bands lying in the visible spectrum were thus found. Now, supposing the first  $m$  bands to lie in the infra-red, the first band visible in the red will be the  $(m+1)$ th, the second the  $(m+2)$ th, . . . and so on, and  $m$  can easily be found from the equations.

$$(m+1)\lambda_{m+1} = (m+2)\lambda_{m+2} = \text{etc.} \dots\dots\dots(1)$$

The products  $(m+1)\lambda_{m+1}$ ,  $(m+2)\lambda_{m+2}$ , etc., gave a series of values for  $K$  whose mean was taken.

The bolometric investigation of the infra-red dispersion followed. The first minimum of the galvanometer deflection indicated the position of the first interference band. Its order  $m$  and the constant  $K$  being known, the corresponding wave-length was given by (1). The positions and wave-lengths of the remaining bands were similarly obtained. The maximum galvanometer

<sup>1</sup>Also for water, bisulphide of carbon, xylol, benzol, quartz, rock-salt, and fluorspar.

deflections were as marked as the minima, and were also utilised for the determinations. The wave-length corresponding to a maximum is  $K/(n + \frac{1}{2})$ , if  $n, n+1$ , be the orders of the two neighbouring minima. Six minima were found in the infra-red for each of the eight glasses, except O. 1092, for which only five were found.

Rubens gives dispersion curves plotted from his measures, with wave-length as abscissa, and index as ordinate. The curve for the glass O. 1151 is reproduced on a reduced scale in fig. 2, 1 mm. representing  $30\lambda - 10\mu$  in one direction, and  $1000n - 1490\mu$  in the other. The five crown glasses show a point of inflexion in

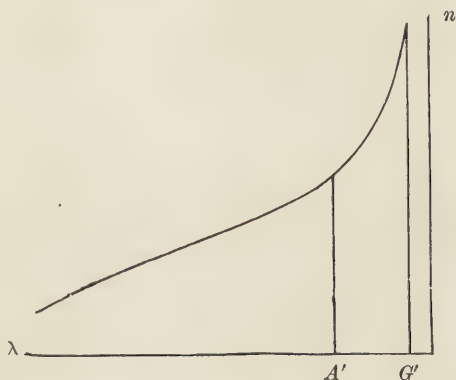


FIG. 2.

the infra-red region, but the flint glasses do not. A later investigation<sup>1</sup> of the dispersion of the flint glass O. 508, with more perfect apparatus, gave, however, a distinct point of inflexion at about  $\lambda = 1.5\mu$ .

**Ultra-violet Spectrum.**—Simon determined the dispersion for all 13 glasses<sup>2</sup> from the  $A'$  line down to the lower limits of wave-length above stated, using prisms of about  $30^\circ$ . In the region, between  $A'$  and  $G'$ , the method of minimum deviation was used. The ultra-violet region was examined photographically by the normal incidence method, using the zinc and cadmium lines.

The zinc, or cadmium, was placed in the crater of the positive

<sup>1</sup> *Annalen d. Physik u. Chemie*, 53, 267 (1894).

<sup>2</sup> Also for quartz, fluorspar, water, benzol, xylol, carbon bisulphide, and  $\alpha$ -monobromonaphthalin.

carbon of an arc lamp, and the bright line spectrum thus produced was photographed on Schleussner plates, by the help of two achromatic objectives of quartz and flourspar, made by Zeiss from Czapski's calculations. A sharp image of the whole spectral region from  $0.360\mu$  to  $0.202\mu$  was formed on one plate. The wave-lengths of the lines in question were known from Cornu's, and Kayser and Runge's investigations. Preliminary trials had shown that the interference method used by Rubens in the infra-red was not suited to the ultra-violet, as the interference bands grew more and more diffuse with the rapidly increasing dispersion. The indices obtained by Simon may be regarded as accurate to the fourth decimal.

Simon, also, has plotted dispersion curves from his observations, with the wave-length as abscissa and index as ordinate. Those for the first nine glasses join on very well to Rubens', except for a slight parallel shift. So far as this shift arises from small errors of observation, Simon claims the greater accuracy for his own determinations.

A summary of the observations is given in the following table by Simon.<sup>1</sup> The first column contains the wave-length in thousandths of a millimetre, the remaining columns the indices. The values for the visible and ultra-violet regions are from Simon's actual observations; the values for the infra-red were obtained from Rubens' determinations, with the aid of graphic interpolation, which was necessary because the wave-lengths employed were not the same for different glasses.

**24. Absorption.** Theory indicates that the dispersion exhibited by a colourless transparent substance is essentially connected with the absorbing powers of the substance for rays in the infra-red and ultra-violet.

Assuming the existence of only two effective absorption bands, one in the infra-red with its centre at  $\lambda_1$ , and the other in the ultra-violet with its centre at  $\lambda_2$ , the elastic-solid theory leads to the equation

$$n^2 = a^2 - \frac{M_1}{\lambda_1^2 - \lambda^2} + \frac{M_2}{\lambda^2 - \lambda_2^2} \dots \dots \dots (1)$$

for the index  $n$  at any intermediate wave-length  $\lambda$ . Rubens has

<sup>1</sup> *Ann. d. Physik u. Chem.*, 53, 555,



[illegible]

shown<sup>1</sup> that his later determinations for the dispersion of the dense silicate-flint O. 500 from  $0.40444\mu$  to  $4.06\mu$  are well represented by equation (1), when the values allotted to its five constants are:  $\alpha^2 = 6.7716$ ,  $M_1 = 1508.2$ ,  $M_2 = 0.03672$ ,  $\lambda_1^2 = 394.65$ ,  $\lambda_2^2 = 0.0404$ . The observations would accordingly be explained on the assumption of a lower absorption band at about  $19.9\mu$ , and an upper one at about  $0.2\mu$ . At any rate, the lower band seems to be a long way below the visible region, and the upper band very near it. Indeed, the yellow tinge of the glass shows that the upper absorption band encroaches on the visible region.

A graphic representation of the dispersion of a glass shows plainly the influence of both absorption bands, if the observations extend far enough into the infra-red. The readiest mode of representation is to plot the curve  $n=f(\lambda)$ , as has been done in fig. 2 (p. 43) for the glass O. 1151.

[The axis of abscissae in the figure runs from right to left for increasing  $\lambda$ , as is shown by  $A'$  being to the left of  $G'$ .]

The dispersion is then measured by  $-dn/d\lambda$ , that is, by the tangent of the slope of the curve. As will be seen from fig. 2, it increases rapidly in passing from the red to the blue end of the visible spectrum; and in the case of flint glass the increase is still more rapid. Thus, in all cases, the influence of the upper absorption band is plainly discernible, as the result of diminishing  $\lambda$  in equation (1) would lead us to expect. On passing from the red to the infra-red, the dispersion at first goes on decreasing, then reaches a minimum (as shown by the point of inflection in the dispersion curve), and then begins to increase again in consequence of the approach to the lower absorption band. It is difficult to estimate the exact position of the point of inflection, as a considerable length of the curve in its neighbourhood is nearly straight. In all the nine curves drawn by Rubens for the glasses which he examined, the effect of the lower absorption band is less conspicuous than that of the upper. In the case of the four flint glasses, the observations would have had to be carried much further in the infra-red to reach the bend at the lower end of the dispersion curve. In the five crown glasses the curve begins to bend just at the last.

On the whole, everything points to the conclusion that the upper absorption band lies decidedly nearer the visible region

<sup>1</sup> *Ann. d. Phys. u. Chem.*, 54, 480 (1895).

than the lower band; and also that in flints the upper band is still nearer and the lower band still further off than in crowns.

The influence of the infra-red absorption is more distinctly brought out by drawing the dispersion curve  $n = F\left(\frac{1}{\lambda^2}\right)$  instead of  $n = f(\lambda)$ , as may be seen from fig. 3, which represents the  $F$  curve for the same glass whose  $f$  curve is shown in fig. 2. The scale of

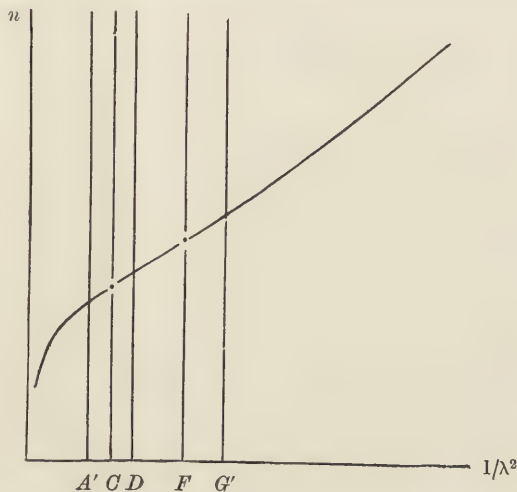


FIG. 3.

ordinates is 1 mm. for  $500n - 740\mu$ , and of abscissae, 1 mm. for  $4/\lambda^2$ , the unit for  $\lambda$  being the thousandth of a mm. as before. The point of inflection of the new curve falls within the visible region, thus leaving room for the dispersive influence of the lower absorption band to display itself in the infra-red. The difference can be explained by means of the identity

$$\frac{d^2n}{d(1/\lambda^2)^2} = \frac{\lambda^5}{4} \left( 3 \frac{dn}{d\lambda} + \lambda \frac{d^2n}{d\lambda^2} \right) \dots \dots \dots (2)$$

Since  $\frac{dn}{d\lambda}$  is negative,  $\frac{d^2n}{d(1/\lambda^2)^2}$  will vanish and become negative before  $\frac{d^2n}{d\lambda^2}$  vanishes and becomes negative, with increasing  $\lambda$ .

Since the point of inflection of the new curve lies in the visible spectrum for crown glasses, and never far beyond it for flints, the

portion of the curve lying in the visible region will never deviate much from a straight line. Hence the simplest form of Cauchy's dispersion formula

$$n = A + \frac{B}{\lambda^2} \dots \dots \dots (3)$$

will be approximately satisfied, especially by the crown glasses.

As the curve  $F$  shows the dispersion relative to  $1/\lambda^2$ , and  $f$  shows it relative to  $\lambda$ , their slopes at corresponding points would be in opposite directions but for the fact that the axis of abscissae runs from right to left in fig. 2. In the interval between their respective points of inflection, the slope of  $f$  increases and that of  $F$  diminishes. Pulfrich,<sup>1</sup> following Sellmeier's example,<sup>2</sup> has used the formula  $n = F(1/\lambda^2)$  in investigating the absorptions in the infra-red and ultra-violet.

**25. Measurement of Absorption.** The absorptions of a number of glasses have been directly determined. The measures relate partly to the visible rays with wave-lengths between  $0.677\mu$  and  $0.436\mu$ , partly to the more refrangible rays between  $0.434\mu$  and  $0.375\mu$ , and partly to the infra-red rays.

**Absorption in the Visible Spectrum  $0.677-0.436\mu$ .** The following observations were made by Müller with Vogel's modified form of Glan's spectrophotometer,<sup>3</sup> and are contained in a paper of Vogel's.<sup>4</sup> They refer to the five glasses O. 340, O. 102, O. 93, O. 203, O. 598; having the running numbers 64, 38, 37, 13, 51 in the list of Art. 17.

The investigation was prompted by the circumstance that the flint O. 340 and crown O. 203 were the glasses selected for the objective of the great Potsdam refractor, and that the other glasses mentioned were to be used in the spectroscope attached to the instrument.

<sup>1</sup> *Ann. d. Physik u. Chem.*, 45, 648 and 664 (1892). See also Winkelmann's *Handbuch d. Phys.*, II. 1, 326.

<sup>2</sup> *Ann. d. Phys. u. Chem.*, 143, 272 (1871).

<sup>3</sup> *Berichte of the Berlin Academy*, March, 1877.

<sup>4</sup> Die Lichtabsorption als massgebender Faktor bei der Wahl der Dimension des Objectivs für den grossen Refraktor des Potsdamer Observatoriums. *Berichte der Berliner Akademie*, Nov. 1896; also *Mathematische u. naturw. Mitteilungen*, 1896, 623.



The thickness  $\beta$  (in millimetres) of each of the glass plates used, and the index for the  $b_1$  line  $\lambda = 0.518\mu$  are here given.

	O. 340	O. 102	O. 93	O. 203	O. 598
$\beta =$	148	100	114.8	141.5	102.5
$n_{b_1} =$	1.5835	1.657	1.632	1.521	1.519

The loss by reflection was calculated by means of Fresnel's formula

$$R = 1 - \left( \frac{n-1}{n+1} \right)^2,$$

$R$  denoting the ratio of the reflected to the incident light for normal incidence on glass of index  $n$ . The value of  $n$  for the  $b_1$  line was used.

The general law of absorption by a given medium for light of given wave-length is, that the quantity of transmitted light diminishes in a *constant ratio* for successive *equal distances* traversed. The ratio of diminution for a variable distance  $x$  may therefore be represented by the expression  $e^{-kx}$ ,  $e$  denoting the base of natural logarithms (2.718). The constant multiplier  $k$  is called the *co-efficient of absorption*. We shall write  $K_x$  for  $e^{-kx}$ ; and, to deduce the transmission through a standard thickness  $a$  from the observed transmission through a thickness  $\beta$ , we have

$$K_a = (K_\beta)^{\frac{a}{\beta}}.$$

Müller reduced his observations to a standard thickness of 10 cm., and thus obtained the following values of  $K_a$  for seven different wave-lengths:

$\lambda =$	0.677	0.580	0.535	0.503	0.477	0.455	0.436 $\mu$
Flint O. 340	0.939	0.878	0.907	0.880	0.880	0.834	0.680
„ O. 102	0.794	0.829	0.808	0.782	0.700	0.663	0.566
„ O. 93	0.943	0.903	0.879	0.871	0.899	0.807	0.714
Crown O. 203	0.903	0.872	0.898	0.872	0.860	0.822	0.806
„ O. 598	0.860	0.818	0.792	0.776	0.771	0.770	0.797

At  $\lambda = 0.436\mu$  the observations were difficult, owing to the faintness in the blue of the petroleum flame employed as source of light. They were therefore repeated by Vogel, whose eyes are very sensitive to blue. He obtained the following values for  $K_a$ :

$\lambda =$		$0.436\mu.$
Flint	O. 340 - - - -	0.706
,,	O. 102 - - - -	0.542
Crown	O. 203 - - - -	0.765
,,	O. 598 - - - -	0.655

For O. 598 there is a striking discrepancy between the two observers. Vogel gets much larger absorption here than Müller, though their observations in the brighter parts of the spectrum were found to agree well.

**Absorption for the more Refrangible Rays  $0.434-0.375\mu$ .**

In the case of the three plates O. 340, O. 102, O. 203, the investigation was carried further up the spectrum by the aid of photography.<sup>1</sup> The values of  $\beta$  and of the index for  $h$  ( $\lambda = 0.410\mu$ ), which was used in calculating the influence of reflection, are:

	O. 340.	O. 102.	O. 203.
$\beta =$	148	100	141.5
$n_h =$	1.601	1.682	1.532

It is noteworthy that the absorption does not increase steadily as the wave-length diminishes, but remains nearly constant over considerable intervals, and then suddenly increases at certain places. This leads to abrupt extinctions of light of certain wave-lengths for certain thicknesses. For example, a plate of light flint O. 340, 10 to 15 cm. in thickness, stops all rays of wave-length less than  $0.370\mu$ . With the heavy flint O. 102 there is a sudden fall in the intensity of the transmitted light near Fraunhofer's line  $H$ .

Further, it was found that a plate about 15 cm. thick of flint O. 340 produced two absorption bands; one faint and diffused, having its centre at  $0.437\mu$ , the other conspicuous, with sharply defined edges, at  $0.4186\mu$ . The breadth of the latter corresponded to a difference of wave-length  $0.0035\mu$ . The latter band also

<sup>1</sup> *Ibid.*, pp. 1226 and 630.

showed itself, but not so strongly, with a plate of crown O. 203 about 14 cm. thick. The heavy flint O. 102 showed no absorption band.

In determining the absorption in the upper part of the spectrum by photographic means, difficulty arises from the fact that, for a given time of exposure, the darkening of the film does not increase in proportion to the intensity of the light, but more slowly. The effect, moreover, varies with the kind of photographic plate employed. In order to avoid this difficulty, Wilsing, to whom the following determinations are due, compared only negatives which had been exposed for equal times to beams of nearly equal intensities. Thus his measures only depend on the assumption that lights of equal intensity produce equal darkening in equal times. By means of Nicol prisms (as in Zöllner's photometer), two beams of different intensity were reduced to the same intensity; and the ratios of reduction being known, the original intensities could be compared. Silver bromide gelatine plates were used. It was found that a difference of 5 per cent. in intensity was appreciable. The following values were obtained for  $K_a$ :

$\lambda =$	0.434	[0.419]	0.400	0.395	0.390	0.375 $\mu$
Flint O. 340, - -	0.569	[0.411]	0.614	—	0.456	0.388
„ O. 102, - -	0.502	—	0.463	0.167	0.025	—
Crown O. 203, - -	0.667	[0.611]	0.695	—	0.583	0.583

The numbers in brackets are interpolated values for the absorption band.

Vogel also endeavoured to determine the absorption of the five glasses in another way.<sup>1</sup> Strips of chloride of silver paper were exposed in sunlight for equal times, immediately in front of and immediately behind the glass plate to be tested. The degrees of darkening were numerically estimated by comparison with a scale prepared by gradually increasing exposures. As the paper could not be fixed and toned, the comparison was made by yellow light. Equal degrees of darkening indicated equal products of intensity and duration. The action of each glass was determined separately,

<sup>1</sup> *Ibid.*, pp. 1228 and 632.

and the glasses were also compared one with another. The following results were derived from a great number of observations :

		$\beta$ .	$K_\alpha$ .
Flint	O. 340	148 mm.	0.526
"	O. 102	100	0.282
"	O. 93	114.8	0.356
Crown	O. 203	141.5	0.589
"	O. 598	102.5	0.604

These values of  $K_\alpha$  are for the portion of the spectrum which acts most strongly on chloride of silver—a portion extending from  $G$  into the ultra-violet; the strongest action being between  $h$  and  $H$ . In calculating the loss by reflection, the values 1.654 for O. 93 and 1.529 for O. 598 were given to  $n_h$ .

Finally, in view of the above-mentioned use to which the two glasses O. 340 and O. 203 were to be put, Vogel gives mean values to exhibit the difference between the visual and the photographic absorptions.

For the visual rays, taking the mean of his own observations and Müller's, he deduces :

Flint O. 340.	Crown O. 203.
$K_\alpha = 0.84$	0.85

For the photographic rays which act upon ordinary bromide of silver gelatine films (their action beginning at  $F$  and extending far into the ultra-violet, with maximum effect between  $H_\gamma$  and  $H_\delta$ ), Vogel adopts the following values and means :

	VALUES OF $K_\alpha$ .	
$\lambda$	Flint O. 340.	Crown O. 203.
0.455 $\mu$	0.83	0.82
0.436	0.69	0.79
0.434	0.57	0.67
0.400	0.61	0.70
$h-H$	0.53	0.59
0.390	0.46	0.58
	Mean, 0.615	Mean, 0.692

**Calculation of Coefficients of Absorption.** From the definition  $K_x = e^{-kx}$ , we have

$$k = -\frac{1}{x} \log_e K_x.$$



Again,  $kx$  will be unity for a thickness  $x=1/k$ ; hence

$$K_{1/k} = e^{-1} = 1/e.$$

$k$  may therefore be defined as the reciprocal of the distance that must be traversed in the absorbing medium to reduce the intensity to  $1/e$  of its original amount;<sup>1</sup>  $k$  is accordingly the reciprocal of a length. Employing the centimetre as unit of length,  $k$  can be deduced from the foregoing tables by the formula

$$k = -\frac{1}{10} \log_e K_a.$$

The following values are thus obtained for  $k$ :<sup>2</sup>

$\lambda =$	0.677	0.580	0.535	0.503	0.477	0.455	0.436 $\mu$
Flint O. 340,	0.0063	0.0130	0.0098	0.0128	0.0128	0.0182	0.0386
„ O. 102,	0.0231	0.0188	0.0213	0.0246	0.0357	0.0411	0.0569
„ O. 93,	0.0059	0.0102	0.0129	0.0138	0.0106	0.0214	0.0337
Crown O. 203,	0.0102	0.0137	0.0108	0.0137	0.0151	0.0196	0.0216
„ O. 598,	0.0151	0.0201	0.0233	0.0254	0.0260	0.0261	0.0227

$\lambda =$	0.434	[0.419]	0.400	0.390	0.375 $\mu$
Flint O. 340,	0.0564	[0.0890]	0.0479	0.0785	0.0947
„ O. 102,	0.0689	—	0.0770	0.3689	—
Crown O. 203,	0.0405	[0.0493]	0.0364	0.0540	0.0540

These figures show that the absorption of the heavy flint O. 102 exceeds that of the other glasses more and more as the wave-length diminishes, and also that its absorption for the longer waves is not surpassed even by the two crown glasses. It is a strongly absorbent glass for the whole spectral region investigated.

At the red end of the spectrum the two flints O. 340 and O. 93 are much less absorbent than the crowns O. 203 and O. 598. At the violet end the case is reversed.

<sup>1</sup> Calculation would be facilitated if 10 were put in the place of  $e$  in defining the coefficient of absorption. The logarithms in the formulae of reduction would then be common logarithms; and the coefficient of absorption would be the reciprocal of the distance in which the intensity is reduced to  $\frac{1}{10}$  of its original amount.—J. D. E.

<sup>2</sup> The figures in brackets relate to the absorption band.

Between the two flints O. 340 and O. 93, as far as the comparison extends, there is not much to choose.

Of the two crowns, O. 598 is more strongly absorbent than O. 203. The coefficient .0227 given for O. 598 at  $\lambda = 436\mu$  is Müller's value, and is probably too small. Vogel's determination is .0423.

### Measurement of Absorption for the Infra-Red Rays.

Rubens has investigated the transparency to infra-red rays of the nine glasses for which he determined the dispersion in the same region.<sup>1</sup> If two plates of thicknesses  $\beta_1, \beta_2$  be placed in turn in the path of a ray, and  $I_1, I_2$  be the intensities after transmission, we easily obtain from equation (2)

$$I_2/I_1 = e^{-k(\beta_2 - \beta_1)}.$$

The ratio  $I_2/I_1$  was determined by bolometric observation, and  $k$  deduced by means of the above relation. The results are given in the following table:

$\lambda =$	0.7	0.95	1.1	1.4	1.7	2.0	2.3	2.5	2.7	2.9	3.1 $\mu$
S. 204	0.00	0.01	0.06	0.10	0.16	0.21	0.37	0.85	1.25	1.73	—
S. 179	—	0.02	0.05	0.10	0.18	0.40	0.71	0.14	1.69	—	—
O. 1143	0.02	—	0.03	—	0.05	0.07	0.11	0.17	0.34	0.75	1.31
O. 1092	0.01	0.04	0.05	0.01	0.01	0.09	0.20	0.34	0.51	0.73	1.24
O. 1151	0.02	—	0.01	0.01	0.02	0.06	0.11	0.23	0.29	0.79	1.15
O. 451	0.00	—	0.01	—	0.02	0.05	0.08	0.18	0.25	0.62	1.09
O. 469	0.00	—	0.02	—	0.01	0.02	0.02	0.03	0.11	0.41	0.69
O. 500	0.00	—	0.00	—	0.00	—	0.00	0.01	0.08	0.30	0.63
S. 163	0.00	—	0.02	—	0.01	—	0.01	—	0.06	0.25	0.51

Taking into account both the magnitude of  $k$  and the distance of the absorbing region from the visible spectrum, the following conclusions are easily drawn. In the infra-red, the borate S. 204 and the phosphate S. 179 are the most strongly absorbent, and the crowns O. 1143, O. 1092, O. 1151, which differ little from one another, come next. The light flint O. 451 occupies an intermediate position between these and the heavy flints O. 469, O. 500, S. 163, which are much less absorbent than the crowns.

<sup>1</sup> *Ann. d. Physik u. Chem.*, 45, 258 (1892).

**26. Comparison of Glasses—Continued.** A comparison of the absorptions of two substances can often be deduced from a comparison of their dispersions in different parts of the spectrum. If dispersion depended exclusively on absorption, a knowledge of the quantities  $\Delta$ ,  $\alpha$ ,  $\gamma$  defined in Art. 17 would suffice to give a clue to the position of at least one of the two absorption regions by the application of the following rule. In comparing two glasses, if one of them has the greater total dispersion and at the same time a relatively large dispersion in the upper portion of its spectrum (especially if accompanied by relatively small dispersion in the lower portion), then this glass has stronger absorption in the ultra-violet than the other. Interchanging the words upper and lower, we obtain the rule for the indication of absorption in the infra-red.

As a matter of fact, dispersion does not depend exclusively upon absorption, but is influenced by other properties, especially by density; but it is usually permissible to regard absorption as the main influence. There is, however, one exceptional case which requires a modification of the above rule. If the larger total dispersion is due to greater density, a larger relative upper dispersion may be an indication of smaller absorption in the infra-red; and in like manner a larger relative dispersion in the lower part of the spectrum may be an indication of less absorption in the ultra-violet. We shall apply these remarks to the principal glasses in the list of Art. 17.

The list contains eight *heavy silicate flints*. Arranged in order of increasing  $\Delta$ , they form the following series: 68, 38, 39, 40, 41, 42, 43, 44, in which the value of  $\gamma$  increases from term to term, and there can be no doubt that this indicates a progressive increase of the upper absorption. It is worthy of note that the mean dispersion increases more rapidly than the simultaneously increasing density. The same remarks apply to the five *ordinary silicate flints*: 34, 35, 36, 37, 67. But in the nine *light flints*, 74, 75, 63, 29, 65, 64, 30, 31, 66, we find that the exclusive influence of the upper absorption is no longer discernible; No. 30 with its small  $\gamma$  is a well-marked instance. It probably owes its high place in the series to its great density. Of the seventeen *crown glasses* 6, 11, 47, 46, 7, 50, 49, 9, 13, 51, 52, 17, 18, 54, 56, 23, 26, the last six form a group in which again the upper absorption increases from term to term. In passing from 17 to 18,



there is perhaps also a diminution of the lower absorption. In the first eleven crown glasses, the dispersion increases very slowly, and the dispersion-ratios  $\alpha$  and  $\gamma$  progress irregularly, so that we can only compare individual members of the series. In passing, for instance, from 11 to 47, and from 50 to 49, there are signs of increase of the lower absorption. Thus it is only in the crowns that infra-red absorption makes its presence evident.

Among the fifteen *barium silicates*, 12, 16, 53, 73, 71, 55, 72, 20, 57, 58, 59, 60, 61, 62, 76, there are four crowns, 12, 16, 71, 20. Density plays an important part in the case of these glasses. The strange fact of two crown glasses, 71 and 20, appearing in the midst of a series of flints would at once suggest this. They evidently owe their place to their great density. The relation of the barium glasses to the silicates may be seen by comparing 12 with 18, 53 with 56, 73 with 23, 20 with 26, 59 with 74. A glance at the accompanying table, in which the density is given under "s," shows that the barium glasses absorb the ultra-violet

	$10^6\Delta$	$10^3\alpha$	$10^3\beta$	$10^3\gamma$	s
12. O. 227. Barium Silicate Crown, -	909	640	703	566	2.73
18. O. 114. Soft Silicate Crown, - -	910	634	705	572	2.55
53. O. 463. Baryta Light Flint, - -	1020	635	706	575	3.11
56. O. 381. Crown of high dispersion, -	1026	629	709	582	2.70
73. O. 846. Baryta Light Flint, - -	1042	631	707	578	3.01
23. O. 152. Silicate Glass, - - - -	1049	628	708	582	2.76
20. O. 202. Densest Barium Silicate Crown,	1092	632	706	573	3.58
26. O. 214. Silicate Glass, - - - -	1102	626	709	584	2.73
59. O. 527. Baryta Light Flint, - -	1133	623	709	582	3.19
74. O. 726. Extra Light Flint, - - -	1142	623	709	586	2.87

rays much less than silicates of only slightly greater dispersion. The fall in dispersion which would *ceteris paribus* accompany diminished ultra-violet absorption is, in this case, largely balanced by the effect of increased density. It is true that a comparison of the partial dispersions of 12 and 18 or of 53 and 56 might lead one to conclude that barium glasses absorb the infra-red rays more strongly than ordinary silicates, inasmuch as their dispersion



at the lower end of the spectrum is greater; and a similar instance is furnished by the comparison of O. 1143 and O. 1151:

	$10^5\delta_1$ .	$10^5\delta_2$ .	$10^5\delta_3$ .
O. 1143. Dense barium silicate crown,	640	704	584
O. 1151. Silicate crown of high dispersion,	634	713	597

But neither Rubens' direct observations on absorption in the infra-red, nor our knowledge of the run of dispersion in that region, indicate any strong infra-red absorption in barium glasses. Hence the facts must be interpreted as showing that in barium glasses the ultra-violet absorption is exceptionally small. This smallness of absorption tends to make the dispersion small, especially at the violet end, while the high density tends to make it large.

Of the six *borosilicates*, 69, 5, 45, 19, 25, 27, only the last two are flints. A comparison of 19 with 12, or of 27 with 61, leaves no doubt that in this group the influence of lower absorption is stronger than in the barium glasses. This is also easily seen by comparing the partial dispersions of 25 and 58:

	$10^5\delta_1$	$10^5\delta_2$	$10^5\delta_3$	$s$
25. O. 164. Borosilicate flint,	710	786	644	2.81
58. O. 543. Baryta light flint,	699	790	650	3.11

The infra-red absorption of the borosilicates is also greater than that of the ordinary silicates. Hence we should expect their ultra-violet absorption to be less, and a comparison of 45 with 6, or of 25 with 74, justifies this inference.

The seven borates, 10, 21, 22, 24, 28, 32, 33 are all flints except the first. Their infra-red absorption is still greater than that of the borosilicates, as will be seen on comparing 10 with 45, 21 with 19, 24 with 25:

	$10^5\Delta$	$10^3\alpha$	$10^3\beta$	$10^3\gamma$	$s$
10 S. 52. Light Borate Crown, - -	840	667	700	555	2.24
45. O. 599. Borosilicate Crown, - -	813	651	701	562	2.48
21. S. 35. Borate Flint, - - -	996	656	702	563	2.56
19. O. 197. Borosilicate Glass, - - -	929	645	704	572	2.64
24. S. 8. Borate Flint, - - -	1129	645	704	571	2.82
25. O. 164. Borosilicate Flint, - - -	1114	637	706	578	2.81

*A fortiori* the infra-red absorption of this group exceeds that of the ordinary and barium silicates. The following are examples:

	$10^5\delta_1$	$10^5\delta_2$	$10^5\delta_3$	$s$
22. O. 252. Borate flint, - - -	667	722	582	2.57
56. O. 381. Crown of high dispersion,	644	729	596	2.70
53. O. 463. Baryta light flint, - -	648	720	586	3.11
32. S. 17. Dense borate flint, - -	990	1128	937	3.51
66. O. 318. Ordinary light flint, - -	960	1124	952	3.48
76. O. 748. Baryta flint, - - -	965	1142	965	3.67

The same thing is shown by comparing 10 with 11, 47, 46, 7, 50, 49; 21 with 56; 22 with 23; 24 with 74; 28 with 65; also 21 with 16, and 24 with 57, 58, 59, 60, 61, etc. It may further be remarked that, in comparing successive terms of the above series of borates, the influence of ultra-violet absorption becomes more and more evident; and that there is no decided indication of infra-red absorption.

The four phosphate crown glasses, 1, 2, 3, 4, having but weak dispersion, do not afford good comparisons. The influence of infra-red absorption is weaker in the first two than in the borates:

	$10^5\Delta$	$10^3\alpha$	$10^3\beta$	$10^3\gamma$	$s$
10. S. 52. Light borate crown,	840	667	700	555	2.24
1. O. 225. Light phosphate crown,	737	658	698	552	2.58
2. S. 40. Med. phosphate crown,	835	654	702	557	3.07

The same remark applies to the phosphate S. 179 when compared with the borate S. 204. In this case the inference is confirmed by the run of their dispersions in the infra-red.

	Dispersion from: $2.0\mu-1.4\mu$	$1.4\mu-0.8\mu$
S. 204. Borate crown, - - -	0.0105	0.0094
	1.12	
S. 179. Medium phosphate crown,	0.0086	0.0079
	1.09	

The numbers 1.12 and 1.09 written underneath are the ratios of the first dispersion to the second. These show that the influence of absorption is not much greater in the borate; a result confirmed by Rubens' values of the coefficients of absorption.

In the very dense barium phosphates, 3 and 4, we again find the small ultra-violet absorption characteristic of barium. Their infra-red absorption is somewhat less than that of the borosilicates.

		$10^5\Delta$	$10^3\alpha$	$10^3\beta$	$10^3\gamma$	$s$
19. O. 197.	Borosilicate glass, -	929	645	704	572	2.64
3. S. 30.	Dense barium phosphate crown, -	884	644	703	565	3.35
4. S. 15.	Densest barium phosphate crown, -	922	641	703	565	3.66

The two barium phosphates would thus seem to be the most transparent of all glasses for the ultra-violet rays.

The five glasses still remaining, namely, the three zinc glasses 70, 15, 48, the lime silicate 8, and the potash silicate 14, do not furnish very definite conclusions. Perhaps, however, from the comparison of 14 with 17, we may infer that the influence of the lower absorption band is even weaker in potash glass than in ordinary silicate crown.

Comparisons of this kind do not lead to clear inferences when the substance of larger  $\Delta$  has the smaller  $\alpha$  and  $\gamma$ , and there is little difference of density. Such an example is furnished by the two silicate glasses 49 and 9.

		$10^5\Delta$	$10^3\alpha$	$10^3\beta$	$10^3\gamma$	$s$
49. O. 567.	Silicate crown, -	859	645	704	569	2.51
9. O. 138.	Silicate crown, -	872	642	704	567	2.53

## 27. Influence of Temperature on the Refraction of Glass.

The index of any substance for a ray of given wave-length alters with the temperature of the substance. In order to estimate the variations correctly, it is necessary to compute the indices relative to air at constant temperature, or to vacuum. Pulfrich<sup>1</sup> investigated the influence of temperature on 12 glasses (as well as on rock-salt, sylvite, quartz, and fluorspar), and showed that the observed temperature-coefficients, which, like those of most solid bodies, present an appearance of great irregularity, had a definite physical significance.

By means of prisms made from the 12 glasses, their indices

<sup>1</sup> *Annal. d. Physik u. Chem.*, 45, 609 (1892).

for the  $D$  line, and dispersions for the three intervals  $CD$ ,  $DF$ ,  $FG'$ , relative to air at the same temperature, were measured (by Abbe's method of a ray returning upon itself). In the first instance the measures were made at the temperature of the room. The values obtained are given in the following table. As the  $A'$

	$n_D$	$10^5\Delta$	$\nu$	$10^5CD$	$10^5\delta_2$	$10^5\delta_3$
					$10^3\beta$	$10^3\gamma$
1. O. 225. Light Phosphate Crown,	1.5160	734	70.3	219	515 701	402 548
2. S. 40. Medium Phosphate Crown,	1.5619	845	66.5	253	592 701	469 555
O. 627. Borosilicate Crown, -	1.5128	806	63.7	241	564 700	449 557
S. 205. Light Borate Crown, -	1.5075	838	60.6	255	583 696	459 548
O. 1022. Silicate Crown, - -	1.5173	860	60.2	254	606 705	475 552
16. O. 211. Dense Barium Silicate Crown,	1.5727	988	58.0	295	693 701	560 567
59. O. 527. Baryta Light Flint, -	1.5718	1130	50.6	329	801 709	658 582
O. 658. Light Borosilicate Flint,	1.5452	1084	50.3	320	764 705	622 574
29. O. 154. Light Silicate Flint, -	1.5710	1324	43.1	382	942 711	789 596
O. 544. Ordinary Silicate Flint, -	1.6130	1652	37.1	472	1180 714	1004 608
42. O. 165. Dense Silicate Flint, -	1.7545	2738	27.6	768	1970 720	1720 628
44. S. 57. Densest Silicate Flint, -	1.9625	4877	19.7	1336	3541 726	3235 663

line, on account of its faintness, was not observed, the dispersion  $\delta$  from  $A$  to  $D$ , and the corresponding ratio  $\alpha$ , are absent from the table, the dispersion from  $C$  to  $D$  being given instead. With this exception, the notation is the same as in the catalogue of Art. 17. Those of the glasses which belong to the catalogue have their catalogue numbers prefixed. It may be remarked that the silicate crown O. 1022 is distinguished, by its small  $\gamma = 0.552$ , from all the silicates in the general list, none of which have  $\gamma$  less than 0.564.

A second set of measures were then made at higher temperature, the prism under examination being enclosed in a steam-heated



chamber. The results gave the amounts by which the indices for the lines *C*, *D*, *F*, *G'* were changed owing to the joint elevation of temperature of the glass and surrounding air. A view of the interior of the chamber was obtained through a glass plate, which was perpendicular to the rays, and therefore produced no deviation. The change of index so found, divided by the corresponding difference of temperature, gives the average change of relative index per degree Centigrade, the air being at the same temperature as the glass. The values thus obtained are reduced to vacuum by multiplying the observed relative index by the absolute index of air at the actual temperature, it being assumed that the absolute index of dry air at 0° C. and 760 mm. is 1.000 294 for all colours, and that for other temperatures and pressures  $n - 1$  is proportional to the density.<sup>1</sup>

Pulfrich's results are contained in the following table. The

	Temperature	<i>C</i>	<i>D</i>	<i>F</i>	<i>G'</i>
O. 225. Phosph. Cr., -	16.6°—99.7°	-0.202	-0.190	-0.168	-0.142
	58.1°	-0.093	-0.080	-0.057	-0.031
S. 40. Phosph. Cr., -	21.0—99.6	-0.314	-0.305	-0.246	-0.237
	60.3	-0.204	-0.194	-0.134	-0.124
O. 627. Bor. Sil. Cr., -	5.8—99.9	0.119	0.137	0.178	0.213
	52.8	0.233	0.251	0.293	0.329
S. 205. Bor. Cr., - -	20.5—99.5	-0.066	-0.074	-0.033	-0.003
	60.0	0.040	0.033	0.075	0.106
O. 1022. Sil. Cr., - -	19.0—99.7	-0.129	-0.105	-0.060	-0.010
	59.3	-0.020	0.004	0.050	0.101
O. 211. Bar. Sil. Cr., -	16.6—99.1	0.021	0.040	0.103	0.142
	57.8	0.132	0.151	0.215	0.255
O. 527. Bar. Fl., - -	17.5—99.2	-0.008	0.014	0.080	0.137
	58.3	-0.103	0.125	0.192	0.250
O. 658. Bor. Sil. Fl., -	19.3—99.2	0.267	0.299	0.356	0.410
	59.2	0.376	0.408	0.466	0.520
O. 154. Sil. Fl., - -	17.9—99.2	0.225	0.261	0.334	0.407
	58.5	0.336	0.372	0.446	0.520
O. 544. Sil. Fl., - -	11.1—99.1	0.244	0.281	0.389	0.503
	55.1	0.360	0.397	0.506	0.621
O. 165. Sil. Fl., - -	13.8—99.6	0.700	0.775	1.051	1.311
	56.7	0.829	0.906	1.182	1.443
S. 57. Sil. Fl., - -	18.5—99.2	1.204	1.449	2.090	2.810
	58.8	1.336	1.588	2.231	2.954

<sup>1</sup> The theory of the experiment is given by Pulfrich in Winkelmann's *Handbuch d. Physik*, II. 1. 308.

column headed "Temperature" contains the temperatures of the two observations and their mean. The columns headed  $C, D, F, G'$  give the average change of absolute index per degree. This is adopted as the true rate of change at the mean temperature. The numbers are given in units of the fifth decimal place, and indicate an increase or decrease (with increasing temperature) according as they are positive or negative. Since the corresponding change of relative index is of practical importance, it is also given, underneath the change of absolute index.

Comparison of the values in the above table shows that the dispersions  $CD, DF, FG'$  always increase with the temperature, whether the indices increase or decrease. The single exception furnished by the interval  $CD$  for the glass S.205 we shall disregard, as due either to some exceptional cause or to a mistake in the observations.

Change of temperature also affects the run of dispersion, as is shown by the following figures, which express the rate of increase (per degree) of the absolute dispersion in millionths of its original amount:

	$CD$	$DF$	$FG'$
O. 225,	55	43	65
S. 40,	36	100	19
O. 627,	75	69	78
S. 205,	-31	70	65
O. 1022,	94	74	105
O. 211,	64	91	70
O. 527,	67	82	87
O. 658,	100	75	87
O. 154,	94	77	93
O. 544,	78	92	113
O. 165,	98	140	151
S. 57,	183	181	223

The inequality of the three numbers for any individual glass indicates that the run of its dispersion has been changed.

**Diminution of Index arising from Diminution of Density with Rise of Temperature.** In attempting a satisfactory explanation of the observed data, the fact must be taken into

account that thermal expansion causes diminution of density, and thus tends to diminish the index. Nevertheless, the indices of many glasses, especially flints, increase with temperature; hence some other cause must be at work which overpowers the influence of density. The following considerations may throw some light on the subject.

The true law of relation between index and density is unknown, but attempts have been made to represent it by empirical formulae, based on the assumption that a certain quantity called the constant of refraction does not vary with changes in density due to temperature. This constant is variously defined by the three following expressions:

$$\frac{n-1}{d}, \quad \frac{n^2-1}{d}, \quad \frac{n^2-1}{n^2+1} \cdot \frac{1}{d},$$

$n$  denoting the index and  $d$  the density.

Employing each of these expressions in turn for calculating the change of index due to mere change of density in heating, and using the observed coefficients of expansion for the glasses in question, Pulfrich found that in no single instance was there an actual diminution of index as large as the calculation gave. Hence it seems probable that, even in the case of those glasses whose indices diminish as the temperature increases, there is some counteracting cause at work tending to increase the index.

This conclusion is confirmed and rendered more definite by the following considerations. According to the first of the three expressions for the constant of refraction, the run of dispersion is not affected by change of density. [ $n_c-1$ ,  $n_D-1$ ,  $n_F-1$ , and their differences  $n_D-n_c$ ,  $n_F-n_D$  would all diminish in the same ratio as  $d$ .] All three expressions agree in making both index and dispersion diminish with increasing temperature. As a matter of fact, however, the dispersion increases. [ $n_c-1$ , etc. increase instead of diminishing, and the dispersions  $n_D-n_c$ ,  $n_F-n_D$  increase.] Thus the additional cause which we have supposed to be at work tending to increase the index, also increases the dispersion, and further, this cause becomes more operative as the blue end of the spectrum is approached.

**Strengthening of Upper Absorption Band with Increase of Temperature.** The above reasoning points to the probability that the upper absorption band grows stronger as the temperature increases, in all glasses, and especially in flints. This would account for the kind of increase that is observed, and would explain the fact that the dispersion always increases, though the change of index is sometimes positive and sometimes negative.

Pulfrich, in fact, drew this conclusion and confirmed it by direct observation. He found that glasses which had only a slight yellow tinge at ordinary temperatures acquired a continually deeper tint when they were heated in porcelain vessels to 200°, 300°, and upwards, up to the melting point (about 400°). The effect, as might be expected, was especially strong in silicate flints; in S. 57 the boiling point of water was sufficient to produce it, and, on the other hand, a cooling mixture of solid carbonic acid dissolved in ether produced marked weakening of the yellow tinge of this glass. When pieces of the glass were strongly heated, they "gradually assumed the colour of dark amber; and when the temperature was reached at which the glass began to soften, it appeared dark red or brown." Spectroscopic examination showed that "even a small thickness of the hot glass stopped all rays of the visible spectrum except a small portion in the red. The original yellow tinge was restored by re-cooling. The experiment could be repeated on the same piece of glass any number of times with the same result, showing that the action was not chemical but purely physical." These experiments at the same time furnished an independent explanation of the fact, observed by F. Vogel, that the index of flint glass changes more rapidly at high than at low temperatures;<sup>1</sup> for the deepening of tint, which occurred on heating the glass S. 57, was much more rapid at the higher temperatures. These results are borne out by phenomena often witnessed at the Jena Glass Works. It may be added that similar phenomena are exhibited by some other substances.

**28. Continuation. Extension of the Observations to Higher Temperatures.** At the suggestion of Pulfrich, the study of the

<sup>1</sup> *Annal. d. Phys. u. Chem.*, 25, 87 (1885).



above-mentioned phenomenon was taken up by J. O. Reed,<sup>1</sup> and extended to temperatures as high as the conditions permitted. Seven glasses were examined (and also the minerals calc-spar, quartz, and fluor-spar). Pulfrich's method was closely followed, but instead of the  $G'$  line, a stronger line  $Hg_{\gamma}$  was used, and denoted by  $G''$ .

The optical characteristics of the glasses experimented on are given in the following table. The values under the headings  $\alpha'$ ,  $\gamma'$  are analogous to  $\alpha$  and  $\gamma$  of the catalogue in Art. 17.

	$n_D$	$10^5 \Delta$	$\nu$	$10^5 CD$	$10^5 \delta_2$	$10^5 FG''$
				$10^3 \alpha'$	$10^3 \beta$	$10^3 \gamma'$
44. S. 57. Densest Sil. Flint, -	1.96249	4885	19.7	1339 274	3546 726	3092 633
S. 163. Densest Sil. Flint, -	1.89035	3994	22.3	1106 277	2888 723	2484 622
42. O. 165. Dense Sil. Flint, -	1.75453	2743	27.5	768 280	1975 720	1646 600
29. O. 154. Light Sil. Flint, -	1.57090	1326	43.0	382 288	944 712	755 576
59. O. 527. Bar. Light Flint, -	1.57171	1136	50.4	332 292	804 709	630 555
16. O. 211. Dense Bar. Sil. Cr.,	1.57270	903	57.6	295 297	698 703	552 555
O.1299. (Like 71. O.1209), -	1.60987	1056	57.4	309 292	747 797	575 544

The five glasses contained in the catalogue have their current numbers prefixed. The values of  $n_D$  are reduced to temperature  $20^\circ$ .

The arrangements for observing at high temperatures are described in detail in Reed's article.<sup>2</sup> The results are calculated in the same way as Pulfrich's, but smaller intervals of temperature are employed; and the result for each interval is assigned to the mean temperature of the interval.

These results are tabulated below. The mean temperatures just referred to are given under  $t_m$ ; the remaining columns contain the corresponding changes of absolute index per degree in units of the fifth decimal place.

<sup>1</sup> *Annal. d. Phys. u. Chem.*, 65, 707 (1898).

<sup>2</sup> *Ibid.*, 711.

	$t_m$	$C$	$D$	$F$	$G''$
S. 57. Dense Sil. Flint.	62°·6	1·218	1·472	2·110	2·800
	156·2	1·579	1·809	2·536	—
	233·0	1·928	2·251	3·212	—
	281·0	1·591	1·911	2·918	—
S. 163. Dense Sil. Flint.	60·5	1·119	1·278	1·752	2·161
	125·5	1·275	1·442	1·959	2·477
	177·5	1·379	1·594	2·098	2·617
	250·5	1·577	1·783	2·396	2·992
	330·0	1·808	2·027	2·753	—
O. 165. Dense Sil. Flint.	57·7	0·703	0·778	1·058	1·294
	126·0	0·916	1·051	1·302	1·668
	176·5	0·960	1·092	1·430	1·714
	231·0	1·127	1·237	1·632	1·993
	280·5	1·277	1·396	1·790	2·140
	325·0	1·382	1·544	1·960	2·405
	379·0	1·758	1·904	2·263	2·893
O. 154. Light Sil. Flint.	58·0	0·226	0·250	0·307	0·360
	149·6	0·324	0·362	0·456	0·548
	251·5	0·509	0·568	0·666	0·768
	351·5	0·577	0·639	0·751	0·870
	436·5	—1·861	—1·720	—1·504	—1·329
O. 527. Bar. Light Flint.	56·5	0·014	0·045	0·107	0·150
	157·1	0·094	0·111	0·179	0·246
	261·5	0·144	0·167	0·249	0·355
	357·0	0·217	0·249	0·350	0·461
O. 211. Dense Bar. Sil. Cr.	61·2	0·024	0·035	0·092	0·099
	154·0	0·096	0·113	0·152	0·186
	259·0	0·156	0·174	0·223	0·258
	358·0	0·221	0·247	0·297	0·340
O. 1299.	55·9	0·394	0·410	0·504	0·528
	148·0	0·419	0·444	0·543	0·577
	251·0	0·455	0·489	0·603	0·629
	356·5	0·509	0·555	0·648	0·682

Further data to assist in drawing conclusions are given in the following summary :

	$t_s$	$T$	$n_D$	$n'_D$	$n_D - n'_D$
S. 57	250°—300°	299°	1·96243	1·96162	81·10 <sup>-5</sup>
S. 163	250—300 ?	364	1·89033	1·89016	17
O. 165	300—330	408	1·75448	1·75434	14
O. 154	380—400	452	1·57089	1·56996	93
O. 527	410—450	406	1·57170	1·57170	0
O. 211	470—490	406	1·57270	1·57270	0
O. 1299	490—500	404	1·60983	1·60983	—1

The second column, headed  $t_s$ , indicates (somewhat roughly) the range of temperature within which softening occurs. In the cases of O. 211 and O. 1299 the temperatures given are those at which any stress present in the glass quickly disappears, and are not softening points in the usual sense; true softening not commencing till a much higher temperature is attained.  $T$  denotes the highest temperature at which observations were made,  $n_D$  the relative index before,  $n'_D$  after heating. The difference of the two is given in the last column.

The observed changes of index, in every case, without exception, tended to increase the three dispersions  $CD$ ,  $DF$ ,  $FG''$ .

The flint S. 57 shows the greatest increase both in index and in dispersion; and the heating of it produced such a large increase in the upper absorption band that the line  $G''$  vanished completely, even at  $100^\circ$ — $120^\circ$ . There is, accordingly, only one observation for this line in the table of experimental results. The rate of increase of index, however, reaches a maximum between  $200^\circ$  and  $250^\circ$ ; and is decidedly lower at  $281^\circ$  than at  $233^\circ$ . Reed suggests, as the explanation, the proximity of the melting point.

For S. 163 the  $G''$  line vanished at a little above  $300^\circ$ . No maximum was observed in the rate of increase of index. The highest temperature to which the glass was exposed was  $364^\circ$ ; and as no sign of softening was here observed, the melting point must have been considerably higher.

The flint O. 165 ranks third as regards index and dispersion, and also as regards increase of absorption. As this glass withstood a temperature of  $408^\circ$  without showing any change of form, its melting point must be much higher.

In the case of the light flint O. 154, the rise of index attains a maximum between the mean temperatures  $250^\circ$  and  $355^\circ$ . The indices begin to decrease during the last observation-interval, the decrease being much more rapid than the previous increase. This suggests that, in the case of S. 57, the maximum met with in the rate of increase of index was the premonitory sign of a reversal, such as has actually taken place in O. 154. The thermal variation of index must be zero for some temperature between  $350^\circ$  and  $400^\circ$ . The increase of dispersion gives no sign of falling off; but, on the contrary, as is shown by the accompanying

figures, grows more and more rapid, and is very large for the final interval.

<i>CD</i>	<i>DF</i>	<i>FG''</i>
24	57	53
38	94	92
59	98	102
62	112	119
141	216	175

There can be little doubt that at the last the glass was not far from its true softening point; and we have thus evidence in favour of the explanation put forward in the case of S. 57.

The three remaining glasses, O. 527, O. 211, O. 1299, exhibit only a slow rise of index, nearly proportional to the rise of temperature. The increase of dispersion is also small, a fact consistent with the weak absorption of these glasses. The spectrum lines remain bright and sharp even at high temperatures. The highest temperatures of observation are still far from the melting point.

The agreement with Pulfrich's previous observations of the five glasses, S. 57, S. 165, O. 154, O. 527, O. 211, is very satisfactory.

The values of  $n_D - n'_D$  show that, in the case of the glasses which were not heated to near the softening point, there was no appreciable change of index. In those which were further heated, the index was diminished, especially in the case of S. 57 and O. 154. It may be mentioned, in explanation, that when optical glasses are freed from stress by "fine-cooling" the index is somewhat raised. When, however, the same glasses are heated anew to the softening point, and then cooled without special precaution, the index is again lowered, and becomes nearly the same as if the glass had been merely cooled in the ordinary way.

**29. Optical Properties of quickly cooled Glasses.** When a lump of glass passes, by rapid cooling, from the plastic to the solid state, the outer portions solidify while the interior is still soft. As the cooling and its attendant shrinkage proceed, the outer layers are brought into a state of thrust and the central



portions into a state of tension. The glass, when it has cooled down, is thus neither optically homogeneous nor optically isotropic; and accordingly produces both curvature of rays and double refraction.

The former action was studied in glass cylinders obtained by pouring melted glass into iron tubes. The double refraction was observed in glass plates, obtained by putting a fragment of clear glass into a fire-clay mould, gradually heating it till it first softened and then ran in the mould, and afterwards cooling it rather quickly.

### **Cylindrical Glass Plates acting like Diverging Lenses.**

Some quickly cooled cylinders were made by Schott (1886) at the request of S. Exner, who, like others before him, had been led, from study of the eyes of animals, to investigate the dioptric properties of cylindrically stratified media.<sup>1</sup> From the mode of preparation of such a glass cylinder, it is natural to suppose that its geometric axis will also be its approximate optical axis of symmetry, and that it will be doubly refracting after the manner of uniaxal crystals, while at the same time showing an increase of index from the axis outwards. Suppose the end of such a cylinder to be ground to a flat surface perpendicular to the axis. A ray of ordinary light incident on this surface will be split into two rays polarised in and perpendicular to the plane through the axis, like the ordinary and extraordinary ray in a uniaxal crystal. This double refraction will be only slightly noticeable if the incident ray is nearly parallel to the axis and the cylinder so short as to be merely a disc. But, in all cases, that ray at least which is polarised in the plane of the axis will follow the same law as a ray of ordinary light in a singly refracting medium stratified cylindrically.

Now it will easily be seen that, according to Huygens' principle, a parallel pencil falling on the whole end surface of the cylinder in the direction of the axis will, owing to bending of the rays within the glass, be rendered divergent or convergent according to the velocity of the light in the outer layers is less or greater than in the inner layers, *i.e.*, according as the index increases or decreases from the axis outwards. For any ray in a plane

<sup>1</sup> Ueber Cylinder welche optische Bilder entwerfen, *Pflügers Archiv f. d. ges. Phys.*, 38, p. 274 (1886), and 39, p. 244 (1886).

through the axis, the curvature at any point is given by the equation

$$\frac{1}{\rho} = -\frac{n'}{n} \cos \phi, \dots\dots\dots(1)$$

where

$$n' = \frac{dn}{dx};$$

$\rho$  being the radius of curvature,  $n$  the index at the point,  $x$  its distance from the axis, and  $\phi$  the angle which the tangent to the ray makes with the direction of the axis. If the index increases outwards, the curved ray is convex to the axis, and  $\rho$  is negative; the opposite is the case if it decreases outwards. A ray incident normally on the end surface of the cylinder will (at least near the point of entrance), be more curved than one obliquely incident at the same point, as is seen from equation (1).

The law of curvature expressed by (1) was first given by Bravais,<sup>1</sup> who deduced it from Huygens' principle, for the case of a medium stratified in parallel planes. An argument against Monge's theory of mirage was removed by it. Bravais' paper being but little known, the law was rediscovered [by James Thomson, who published it at the British Association meeting in 1872; and numerous consequences were shortly afterwards deduced from it by Everett,<sup>2</sup> who discussed its application to cylindrical stratification.]<sup>3</sup>

If, from a glass cylinder in which index is a function of distance from the axis, a plate be cut having its faces perpendicular to the axis, this plate will act as a dispersive or collective lens, according as the index increases or diminishes outwards. When a pencil of parallel rays is incident normally, the curvature impressed on the rays within the plate takes the place of the deviation due to the prism-like action of an ordinary lens. As shown by Exner,<sup>4</sup> the analogy between lens and plate is complete when the index satisfies the relation

$$n = n_0 + cx^2, \dots\dots\dots(2)$$

where  $n_0$  is the value of  $n$  at the axis, and  $c$  is a constant. In

<sup>1</sup> *Annales de Chim. et de Phys.*, 46, 492 (1856).

<sup>2</sup> [See two papers in *Phil. Mag.*, 1873, and *Deschanel*, Part. IV.]

<sup>3</sup> [The original cites continental rediscoveries of much later date.]

<sup>4</sup> Compare conclusion of paper quoted above, and another "Linsenkirkung nicht homogener Körper," *Ann. d. Phys. u. Chem.*, 28, 111 (1886).

this case the image formed by the plate of a bright point on its axis will have the same degree of sharpness as in the case of a lens, and the well known lens formula, connecting the distance of object and image with the focal length, will hold unchanged for the disc. In the case of the disc, the focal length will depend on the thickness  $e$  of the plate and the constant  $c$ , the law<sup>1</sup> being

$$f = -\frac{1}{2ce}, \dots\dots\dots (3)$$

Quickly cooled glass cylinders only give dispersive plates, as in them  $c$  is always positive. Fig. 4 illustrates Exner's proof of the formula for collective plates.

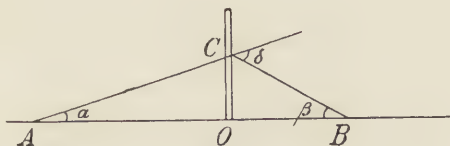


FIG. 4.

$OC$  is the plate,  $AB$  the axis,  $AC$  the incident,  $CB$  the emergent ray. The thickness of the plate is neglected. We have

$$\alpha + \beta = \delta.$$

If  $\alpha, \beta$  are small angles, and  $AO = a$ ,  $OB = b$ , we may put

$$\alpha = \frac{x}{a}, \quad \beta = \frac{x}{b}.$$

From (1) 
$$\delta = -en',$$

and hence 
$$\frac{x}{a} + \frac{x}{b} = -en'.$$

Now if relation (2) holds,  $n' = 2cx$ , and therefore

$$\frac{1}{a} + \frac{1}{b} = -2ce.$$

<sup>1</sup> [This can be proved as follows. For rays of small inclination to axis, (1) gives  $\frac{1}{\rho} = -\frac{n'}{n}$ , which by (2) is  $-2cx/n$ . Angle between initial and final directions in glass  $= e/\rho = -2cex/n$ . Angle between incident and emergent rays in air  $= -2cex$ . This must be equal to  $x/f$  if  $f$  is focal length of equivalent lens. Hence  $1/f = -2ce$ .]

Counting distances measured in the direction in which light travels as positive, and those in the opposite direction as negative, and substituting from (3), we obtain finally

$$\frac{1}{b} - \frac{1}{a} = \frac{1}{f}$$

**Double Refraction of quickly cooled Glass Plates.** Glass cylinders, such as these we have just been describing, when placed between crossed nicols in parallel light, give concentric coloured rings like those which a uniaxal crystal plate cut perpendicular to the axis shows with divergent light. The appearance is, however, less regular, and is disturbed by the veins which are always present in the cylinders, especially if the thickness is considerable. Czapski therefore chose quickly cooled glass plates instead of cylinders for investigating double refraction.<sup>1</sup>

The plates were prepared in the manner described above. Using only very simple apparatus, consisting of a collimator, a telescope, and two nicols, he arrived at practically the same results as were previously obtained by Kerr<sup>2</sup> in a similar investigation with more elaborate appliances.

The collimator and telescope, each of 36 mm. aperture, and 380 mm. focal length, are placed horizontal and directly pointing at one another. The glass plate to be examined is laid between them in a horizontal position, with two opposite edges at right angles to the common axis of telescope and collimator. These edges are ground and polished so as to form parallel vertical planes. In the focal plane of the collimator is a horizontal slit, before which the polariser is placed with the plane of polarisation inclined to the horizon. The telescope, adjusted for infinity, is directed upon the slit, which is illuminated by a lamp. The eyepiece of the telescope is then removed, the analyser inserted in its stead, and the draw tube pushed in to enable the eye to be placed at the focus of the objective. With crossed nicols, a series of approximately straight and horizontal interference bands will then be seen, showing vivid colouring with white light. In each half (upper and lower) of the field there is one dark uncoloured band, and the coloured ones are symmetrical with regard to it.

<sup>1</sup> *Annal. d. Phys. u. Chem.*, 42, 319 (1891).

<sup>2</sup> *Phil. Mag.*, 26, 321 (1888).



With monochromatic (sodium) light the bands seen are alternately bright and dark. In both cases they are broadest at the centre.

This experiment teaches that a quickly cooled glass plate is made up of a number of optically dissimilar layers approximately parallel to its faces. A ray of light on entering any layer is split into two, polarised parallel and perpendicular to the plate. Let  $n_p$  and  $n_s$  be the indices of the two polarised rays. In the middle layer of the plate  $n_p < n_s$ , and as we travel outwards towards the surface  $n_p$  increases faster than  $n_s$ . In the layer giving rise to the dark band with white light  $n_p = n_s$ , and it may therefore be called the neutral zone. In the layers outside it  $n_p > n_s$ . If  $q$  be the number of dark bands in either half of the plate with monochromatic light, we have

$$(n - n_0)_p - (n - n_0)_s = q \frac{\lambda_0}{D} \dots\dots\dots (4)$$

where  $n$  is the index of the external layer,  $n_0$  of the central layer,  $\lambda_0$  the wave-length in air,  $D$  the breadth of the plate between its polished edges, and the subscripts  $p$  and  $s$  denote that the light is polarised parallel and at right angles to the plate respectively.

Each of the two neutral zones behaves like a singly refracting medium between crossed nicols, a fact which explains the presence of the corresponding dark band.

The next dark band on the outer side is given by

$$\frac{D}{\lambda_p} - \frac{D}{\lambda_s} = 1, \dots\dots\dots (5)$$

and on the inner side by

$$\frac{D}{\lambda_p} - \frac{D}{\lambda_s} = -1, \dots\dots\dots (6)$$

$\lambda_p, \lambda_s$  denoting in either case the wave-lengths of the components polarised parallel and at right angles to the plate in the layer bordering the neutral zone. For, when the difference of phase of the two perpendicularly polarised rays amounts to a whole wave-length, they will combine in the same way as if the phase difference were zero; and the same is true for a difference of phase amounting to any whole number of wave-lengths. The complete series of dark bands is therefore obtained by substituting the numbers 2, 3, ... for 1 in equations (5) and (6). Now if  $\lambda_0$  be the wave-length of a ray of monochromatic light in air, the wave-length  $\lambda$  in a medium whose index is  $n$  is given by  $n\lambda = \lambda_0$ .

Substituting for  $\lambda_p, \lambda_s$ , in equations (5) and (6) by means of this relation, equation (4) is easily obtained.

The optical results just described correspond to what we should expect on considering the manner in which such a glass plate passes from the soft to the rigid state. The internal layers must be in a state of tension, the outer of compression (or thrust); hence between the two there must be an intermediate layer free from stress.

The differences  $(n - n_0)_p$  and  $(n - n_0)_s$  on the left-hand side of equation (4) may also be determined independently by a dioptric method. Suppose the eyepiece replaced in the telescope, the analyser having been withdrawn, and let the polariser be placed with its principal section parallel to the glass plate, *i.e.* horizontal. On adjusting the telescope for infinity it will be found that the image of the slit is not in focus; for a parallel incident pencil becomes divergent on traversing the plate. Let  $e_p$  be the distance the eyepiece must be pulled out in order to get a sharp image, and let  $e_s$  be the corresponding distance when the principal section of the polariser is at right angles to the plate, *i.e.* vertical. If  $e_p$  and  $e_s$  be measured, the two required differences can then be calculated from the formulae:

$$\left. \begin{aligned} (n - n_0)_p &= \frac{r^2}{2fD} \cdot \frac{e_p}{f + e_p} \\ (n - n_0)_s &= \frac{r^2}{2fD} \cdot \frac{e_s}{f + e_s} \end{aligned} \right\} \dots\dots\dots (7)$$

$2r$  being the thickness of the plate, and  $f$  the focal length of the telescope objective.

The following is the proof. Putting  $r$  for  $x$  in equation (2), and  $D$  for  $e$  in equation (3), we have

$$\begin{aligned} c &= \frac{n - n_0}{r^2}; \\ -f &= \frac{1}{2cD} = \frac{r^2}{2D(n - n_0)}. \end{aligned}$$

The distances  $F_p, F_s$  of the centres from which the rays diverge after transmission through the plate are therefore

$$F_p = \frac{r^2}{2D \cdot (n - n_0)_p}, \quad F_s = \frac{r^2}{2D \cdot (n - n_0)_s} \dots\dots\dots (8)$$

Since both  $F$ 's are (on account of the smallness of  $n - n_o$ ) large compared to the distance of the glass plate from the objective, they may also be regarded as the distances from the objective. Hence we have

$$\frac{1}{f + e_p} + \frac{1}{F_p} = \frac{1}{f}, \quad \frac{1}{f + e_s} + \frac{1}{F_s} = \frac{1}{f} \dots \dots \dots (9)$$

If we eliminate  $F_p$  and  $F_s$  from equations (8) and (9), we arrive at equations (7). The process which has here been employed differs somewhat from Czapski's, which does not lend itself to a short summary; the numerical results, however, are scarcely affected by the change.

The following table contains three sets of observations and the values deduced for  $\Delta_p = (n - n_o)_p$ ,  $\Delta_s = (n - n_o)_s$ , and  $\Delta_p - \Delta_s$ . Set *A* relate to a circular disc of crown glass; set *B* to the same disc, with the outer layers as far as the two neutral zones screened off, so that here  $n - n_o$  denotes the difference of indices of the neutral zone and the mid-layer. Set *C* relate to a rhomb of flint glass. The quantities given are the means of numerous observations made at different times. Lengths are given in millimetres, and for the wave-length of the sodium light employed the value  $\lambda_o = 5893 \times 10^{-7}$  mm. is assumed.

	<i>D</i>	<i>2r</i>	<i>q</i>	<i>e<sub>p</sub></i>	<i>e<sub>s</sub></i>	$10^7 \Delta_p$	$10^7 \Delta_s$	$10^7 (\Delta_p - \Delta_s)$	$10^7 (\Delta_p - \Delta_s)$
						From eqns. (7).			From eqn. (4).
<i>A</i>	110	26	8	18.0	9.0	914	468	446	429
<i>B</i>	110	15	3	18.0	9.0	304	156	148	161
<i>C</i>	156	36	9	21.5	17.0	1463	1170	293	339 <sup>1</sup>

The values obtained by the two independent methods are in fair agreement, and afford useful information with regard to the refracting properties of quickly cooled glass. It will be noticed that for the crown glass  $\Delta_p$  is about twice as great as  $\Delta_s$ .

#### Disappearance of Double Refraction on heating the Glass.

If glass in a state of stress is kept for some time at a high temperature, the stresses gradually disappear. Although this process involves permanent displacement of elementary portions,

<sup>1</sup> This result was calculated from the stated number  $q = 9$ . Apparently Czapski has used the value  $q = 8$  instead, which gives 302.

it begins at temperatures much below those at which softening, in the usual sense of the word, takes place. In studying the conditions for cooling optical glasses without the production of stress, Schott endeavoured to determine for each glass the lowest temperature at which relief of stress began to show itself by diminution of double refraction.<sup>1</sup>

He employed glass cylinders 10-15 mm. in diameter and 20-40 mm. in length, with their ends plane polished to admit of clear vision through. The number of coloured rings shown by such a cylinder between crossed nicols increases with the amount of stress. Thus, if a glass cylinder on being heated shows fewer rings than before, a diminution of stress may be inferred. In Schott's experiments the heating was carried on in a thermo-regulator which permitted temperatures of 350°—477° to be maintained.

Five glasses were examined, namely, ordinary crown 682, ordinary flint 672, borosilicate crown 792, Jena normal thermometer glass 16<sup>III</sup>, and the borosilicate thermometer glass 59<sup>III</sup>. The lowest temperatures at which there was an undoubted diminution in the number of rings were :

Crown 682,	-	-	-	-	400°—410°
Flint 672,	-	-	-	-	350 —360
Borosilicate crown 792,	-	-	-	-	400 —410
Thermometer glass 16 <sup>III</sup> ,	-	-	-	-	400 —410
Thermometer glass 59 <sup>III</sup> ,	-	-	-	-	430 —440

The time of exposure to the given temperatures was 20—24 hours. Exposure to lower temperatures for the same time had no effect, while higher temperatures made more rings vanish, *i.e.* acted more quickly. Schott remarks that lower temperatures might possibly have produced an effect if allowed sufficient time.

The temperature at which the effect becomes noticeable is higher or lower according to the melting point of the glass in question. As there are glasses more fusible than flint 672, and others less fusible than borosilicate 59<sup>III</sup>, it is to be assumed that diminution of double refraction may begin below 350° or above 440°.

In the case of optical glasses, these observations are of importance, as indicating the temperature in the neighbourhood of which

<sup>1</sup> *Zeitschr. f. Instrumentenk.*, 11, 330 (1891).



cooling must be most cautiously regulated for the complete removal of stress. The application of the results to thermometer glasses will be discussed later.

**30. Testing Lenses and Plates by Polarised Light.** A positive lens can easily be tested for the presence and character of stress in the manner illustrated in fig. 5.<sup>1</sup>

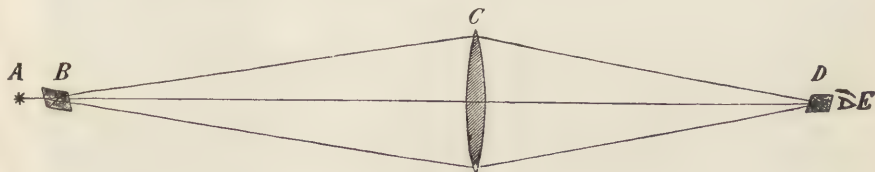


FIG. 5.

*A* is the source of light (a paraffin lamp), *C* the lens, and *E* the eye, *A* and *E* being conjugate foci. *B* and *D* are two Nicol's prisms set parallel to start with. The distances being adjusted so that the lens appears filled with light, the Nicols are then crossed. If the lens is free from stress the field will now appear dark; but if not, there will still be illumination. If the stress is of a symmetrical kind a black cross will be seen on the bright field; if irregularities are present, the cross will be distorted. To examine the cross in all positions, the Nicols should be rotated and not the lens, as the warmth of the hand might cause local disturbance.

In testing plane discs for objectives, a slightly different arrangement is employed, which is represented in fig. 6. Here *S* is a concave mirror, and *A* and *E* are on opposite sides of its centre of curvature.

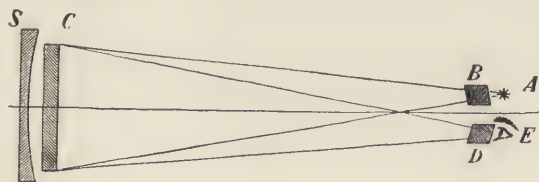


FIG. 6.

A moderate amount of symmetrical stress means a slow increase of index from axis to circumference. It has no injurious

<sup>1</sup> Communication from the Glastechnisches Laboratorium, Jena, Dec., 1889.

effect. Irregular stress, on the contrary, produces capricious variations of refracting power.

Glasses with irregular stresses are not suitable for objectives of any considerable size. If the defect is very slight it can be partially compensated by tentative deviations from the spherical form in polishing.

The fine-annealing process renders it possible to obtain objective discs of diameters up to 35 cm. almost entirely free from stress. With the ordinary cooling process, discs of 12 cm. diameter generally show the black cross indicative of stress.

**31. Elliptic Polarisation of Light reflected from Glass Mirrors.** According to Fresnel's theory a plane polarised ray after reflection at the surface of a transparent body is again plane polarised; and as the angle of incidence (for a ray of constant azimuth) increases from  $0^\circ$  to  $90^\circ$ , the plane of polarisation approaches the plane of incidence, coincides with it at the polarising angle, and then passes beyond it. If we suppose the reflected ray to be resolved into two components  $P$  and  $S$ , polarised parallel and perpendicular to the plane of incidence,  $R_p$  and  $R_s$  being the corresponding amplitudes, then, according to the theory,  $R_s$  continually diminishes as the angle of incidence increases, vanishes at the polarising angle, and afterwards becomes negative. If the amplitudes be regarded as essentially positive,  $R_s$  attains a minimum value zero, and at the same time  $S$  undergoes a change of half a period in phase. No other phase-difference between  $P$  and  $S$  is recognised by the theory.

It has been known since the observations of Airy and Jamin that Fresnel's theory is not in exact agreement with facts. The component  $R_s$  reaches at the polarising angle a minimum value different from zero, and the difference of phase introduced between  $P$  and  $S$  varies with the angle of incidence, increasing from 0 to a  $\frac{1}{2}$  period as the angle increases from  $0^\circ$  to  $90^\circ$ . For the polarising angle the difference is a  $\frac{1}{4}$  period. Thus the light is generally elliptically polarised, and the polarising angle is merely the angle at which the axes of the ellipse are parallel and perpendicular to the plane of incidence.

Jamin, in discussing surface reflection, calls surfaces positive or negative according as  $P$  is earlier or later in phase than  $S$ . In this sense glasses are generally positive.

Cauchy has advanced a theory regarding this elliptic polarisation which starts from the assumption that at reflection (and refraction) longitudinal vibrations are also set up, which, however, are quickly extinguished. In his formula connecting the difference of phase between  $P$  and  $S$  with the angle of incidence, the only constants which enter are the index and the so-called coefficient of ellipticity of the reflecting substance. Thus the whole phenomenon is made to depend upon the optical natures of the two media at whose boundary reflection occurs.

It has since been shown by various authorities that the phenomena in question might be explained as effects of a very thin layer clinging to the reflecting surface. In the case of glass mirrors especially, the presence of a film due to the polishing has been suggested. As a matter of fact it is found that the phenomena vary with the mode of preparation of the surface. Some difficulties in Cauchy's theory are avoided by this supposition.<sup>1</sup>

K. E. F. Schmidt, without committing himself to any theory, has described experiments by which he attempted to actually determine whether the surface layer originates the elliptic polarisation, or merely modifies it.<sup>2</sup> His reflecting surfaces were the faces of  $30^\circ$  prisms made of calspar, light silicate flint O. 154 (29), dense silicate flint O. 604, silicate crown O. 20 (11), and dense barium silicate crown O. 1267.

The image of an electric arc was thrown, by means of the condenser and two projection lenses, on a slit at the focus of a collimating lens of 25 cm. focus. The rays emerging from the lens as a parallel beam traversed the polariser, and then fell on the reflecting surface. After reflection they passed through a quartz plate 0.4887 mm. thick, set at right angles to their path. The plate was cut parallel to the optic axis, and was set with this axis at right angles to the plane of reflection. The light next passed through the analyser, then through a direct vision train of prisms, and finally through a lens of 40 cm. focus by which it was thrown on a photographic plate.

In this arrangement the  $S$  component of the reflected light forms the ordinary and the  $P$  component the extraordinary ray in

<sup>1</sup> Compare the paragraph "Modification of Reflection Phenomena by Surface Films" by P. Drude in Winkelmann's *Handb. d. Phys.*, II. 1, 761.

<sup>2</sup> Ueber die ellipt. Polar. im reflektierenden Lichte. *Annal. d. Phys. u. Chem.*, I. Teil: 51, 417; II. Teil: 52, 75 (1894).

the quartz plate. Hence in passage through the plate  $S$  gains on  $P$  by

$$\frac{(n_p - n_s) \cdot d}{\lambda}$$

vibrations,  $n_p$  and  $n_s$  being the indices of the two components,  $d$  the thickness of the plate, and  $\lambda$  the wave-length in air. If now, by the act of reflection, a gain  $\epsilon$  of  $P$  over  $S$  is introduced, we shall have for the whole gain of  $S$  over  $P$

$$\frac{(n_p - n_s) \cdot d}{\lambda} - \epsilon$$

wave-lengths. Putting this equal to  $\frac{m}{2}$  we get

$$\lambda = \frac{(n_p - n_s) \cdot d}{\frac{m}{2} + \epsilon} \dots \dots \dots (1)$$

Light of the wave-length obtained from this equation by assigning any integral value to  $m$  will again be linearly polarised after reflection. If its plane of polarisation be perpendicular to that of the analyser it will be extinguished by the latter, and a dark band will appear in the spectrum at wave-length  $\lambda$ . Schmidt denotes this band by its order  $m$  printed in Roman numerals. If the reflecting substance be removed, the bands of even order will be seen when the nicols are crossed, those of odd order when they are parallel. The reflection causes a rotation of the plane of polarisation, and hence if the analyser be fixed permanently at  $45^\circ$  to the plane of incidence, the interference bands will appear for a certain azimuth of the polariser depending on the angle of incidence.

If we take as reference point, for an interference band of given order  $m$ , the position it occupies in the spectrum when  $\epsilon = 0$ , we see from equation (1) that a positive  $\epsilon$  shifts the band towards the violet, and a negative  $\epsilon$  towards the red. The greater the absolute value of  $\epsilon$  the difference of phase, the greater the displacement. For measuring the displacements of the bands on the photograph, Schmidt used the cyanogen lines to set by; his measures refer to the bands of orders xvii., xix., and xxi.

Many different ways of polishing the glass reflector were tried, and the consequent changes in the position of the interference bands recorded photographically. With the flint glasses O. 154 and O. 604, the experimenter succeeded on several occasions in



bringing the same bands repeatedly to the same places in the spectrum, by stripping off gelatine from the surface. (A layer of liquid gelatine is poured on the glass surface, allowed to dry, and then pulled off. The process is due to Wernicke.<sup>1</sup>) Schmidt infers that  $\epsilon$ , the gain in phase of  $P$  over  $S$  corresponding to this permanent position of the interference bands, does *not* originate in a foreign surface film, and supports this conclusion by further arguments and practical tests. The fact that the gelatine process had not always the desired effect may be explained by chemical action, to which the crown glasses, for example, would be specially liable. The conclusion is thus arrived at that the elliptic polarisation of light reflected from a polished glass surface is due to an inherent property of the glass, though modified by the introduction of foreign matter in polishing.

**Variation of the Difference in Phase between  $P$  and  $S$  with Angle of Incidence.** After these preliminary experiments, Schmidt measured for 11 glasses the gain in phase of  $P$  over  $S$  in the reflected light for various angles of incidence. He used the method described above, the reflecting surfaces being first repolished and cleaned by stripping off gelatine. With a view to determining the phase difference  $\epsilon$  from the corresponding position of the interference bands in each case, the displacement of the bands was calibrated by means of a Soleil's compensator.

The following data are given for the glasses examined,  $n_F$  denoting the index for the  $F$  line,  $\Delta$  the mean dispersion from  $C$  to  $F$ , and  $\phi_F$  the polarising angle for light from the  $F$  line:

		$n_F$	$10^5 \Delta$	$\phi_F$
11.	O. 20. Silicate Crown, - - - -	1.5078	824	56°.3
	O. 671. Silicate Crown, - - - -	1.5224	904	56.6
	O. 1243. Soft Silicate Crown, - - - -	1.5278	1012	56.8
29.	O. 154. Light Silicate Crown, - - - -	1.5804	1327	57.5
	O. 1020. Ordinary Light Flint, - - - -	1.6227	1647	58.35
	O. 524. Ordinary Silicate Flint, - - - -	1.6330	1710	58.5
	O. 604. Dense Silicate Flint, - - - -	1.6860	2104	59.10
	O. 1288. Dense Barium Silicate Crown, - - - -	1.5796	995	57.7
	O. 1267. Densest Barium Silicate Crown, - - - -	1.6202	1092	58.3
59.	O. 227. Baryta Light Flint, - - - -	1.5798	1133	57.7
	S. 169. Phosphate Crown, - - - -	1.5261	747	56.8

<sup>1</sup> *Annal. d. Phys. u. Chem.*, 30, 461 (1887).

The measures were for the bands xix. and xxi. Since xix. is near *F*, and xxi. near *G*, the differences of phase are for green and blue light. The precise wave-lengths, which vary from one observation to the next, are given by equation (1).

The values obtained for the four silicate flints at band xxi., that is, for blue light, are shown in the following table:

	O. 154	O. 1020	O. 524	O. 604
20°		0	3	5
30	0	5	6	10
35	0	9	—	15
40	8	—	15	20
45	12	20	17	—
47	19	—	—	—
50	31	45	23	—
50·3	—	—	—	58
53	—	—	56	—
53·3	—	—	—	98
53·7	—	71	—	—
55	105	—	—	—
55·7	—	124	—	—
56	—	—	165	—
56·7	—	188	—	—
60	72	121	—	155
61	63	112	58	130
62	—	—	43	—
63	—	60	—	99
64	—	—	36	—
65	32	45	—	72
68	23	—	20	49
70	19	27	17	37
72	—	—	—	30
73	—	—	—	24
75	—	—	—	23
80	6	—	—	—

The angle of incidence is given in the first column; the remaining columns give the deviations of the glasses from Fresnel's theory, according to which  $\epsilon$  is zero for angles of incidence less than the polarising angle, and half a wave-length for angles of incidence greater than the polarising angle. The quantity given in the table is  $1000\epsilon$ , or  $1000(\frac{1}{2} - \epsilon)$ , according as the angle of

incidence is less, or greater, than the polarising angle. Taking, for example, O.154, at incidence  $50^\circ$  the gain of  $P$  upon  $S$  is  $0.031\lambda$ , and at  $60^\circ$  is  $0.5 - 0.072 = 0.428\lambda$ .

Schmidt gives the name *region of ellipticity* to the region (extending on both sides of the polarising angle), within which the deviations from Fresnel's law are large enough to be measurable; and he finds that the greater the extent of this region the larger are the deviations which it comprises. The extent of the region, and the average magnitude of the deviations within it, jointly determine the ellipticity of the glass in question. Thus, of the four flint glasses, the light flint O.154 has the least ellipticity for blue light, and the heavy flint O.604 the greatest. The results for green light are nearly the same. The ellipticity of the three silicate crowns is much less than that of the flints, deviations being only observed close to the polarising angle, and then amounting only to a few thousandths of a wave-length. According to observations not quoted here, O.20 is positive, in Jamin's sense, for blue and green light below the polarising angle, but negative above it; O.671 is almost neutral for blue light, and negative for green; O.1243 is negative for green light below the polarising angle, positive above. The three baryta glasses examined are positive; the baryta light flint O.527 shows less ellipticity than the light silicate flint O.154 and also than the baryta crown O.1267, while crown O.1288 again shows very little ellipticity. Phosphate crown S.169 also is only slightly elliptic.

## CHAPTER III.

### PERFECTING OF OPTICAL SYSTEMS BY THE NEW GLASSES. THE MICROSCOPE.

**32. Numerical Aperture and Limits of Performance of the Microscope.** Let  $u$  be the semivertical angle of the cone of rays which the objective is able to admit from a point of the object, and  $n$  the index of refraction of the intervening medium. Then if we put

$$a = n \sin u, \dots\dots\dots(1)$$

$a$  is called by Abbe the *numerical aperture* of the objective. The vertical angle  $2u$  of the cone of rays is sometimes called the *angular aperture*, or simply the *aperture*; but the *numerical aperture* (abbreviated into N.A.) is much more important in the theory of the microscope. In order that it may be possible to represent distinctly in the microscopic image the structure of the object, the fineness of the structure must not exceed a certain limit. This limit, which was pointed out almost simultaneously by Abbe<sup>1</sup> and von Helmholtz,<sup>2</sup> depends only on the numerical aperture of the objective and the wave-length of the light employed. For a regular structure, such as a fine grating, the limit can easily be stated. If the common distance of the lines from centre to centre is

$$d = \frac{\lambda}{2a}, \dots\dots\dots(2)$$

<sup>1</sup> *Archiv für mikroskop. Anatomie*, 9 (1874).

<sup>2</sup> *Annal. d. Phys. u. Chem. Jubelband*, 557 (1874).



$\lambda$  being the wave-length in air, it is just possible to make the structure visible in the microscope by oblique illumination. If the distance be less than this the grating will not be resolved.

Since the angular aperture  $2u$  is necessarily less than  $180^\circ$ ,  $a$ , the numerical aperture, is less than the index of the intervening medium, and thus, in a dry system, is less than 1. The greatest aperture hitherto attained in an immersion system is 1.60. If for  $\lambda$  we substitute  $0.55\mu$ , which is the wave-length of the brightest rays, we find that the limiting fineness of resolvable structure for a dry system is given by  $d = 0.275\mu$ , and that  $d = 0.172\mu$  is the utmost limit of microscopic resolvability.

**33. Useful Magnification.** When the microscope is adjusted for the "nearest distance of distinct vision"  $l$ , the distance  $d$  between lines which are barely resolved is seen under the angle

$$\epsilon = \frac{md}{l},$$

$m$  denoting the magnification. If we substitute for  $d$  from equation (2), and solve for  $m$ , we find

$$m = \frac{2l\epsilon}{\lambda} a.$$

For microscopic observation  $\epsilon$  must be at least  $2'$ , and  $\epsilon = 4'$  is ample for comfortable vision. Inserting these values in turn, and putting  $l = 25$  cm.,  $\lambda = 0.55\mu$ , the following values are obtained for  $m$ :

$$m_1 = 529a,$$

$$m_2 = 1058a.$$

Magnifications much less than  $m_1$  do not utilize the full capabilities of the aperture; those exceeding  $m_2$  are futile as revealing no further detail. Thus the useful powers are those between  $m_1$  and  $m_2$ .

**34. Magnification by Objective and Amplification by Eyepiece.** Let  $f_1$  be the *upper focal length* of the objective [the distance from the upper principal point to the upper principal focus],  $f_2$  the upper focal length of the eyepiece,  $l$  the *visual distance* [least distance of distinct vision], and  $t$  the optical tube-

*length*, that is, the distance from the upper principal focus of the objective to the lower principal focus of the eyepiece. Then the magnification  $m$  of the microscope can be shown to be expressible as

$$m = \frac{l}{f_1} \cdot \frac{t}{f_2}.$$

The first factor  $\frac{l}{f_1}$  is the magnification which the objective would give if used as a simple magnifier, and is called the *magnification by the objective*. The second factor  $\frac{t}{f_2}$  is called the *amplification by the eyepiece*. The so-called *finder eyepiece* has amplification unity.

**35. Aberration-Constant of Objective.** The image formed by the objective is limited in fineness of detail by the numerical aperture, as above stated. It also has defects due partly to imperfections of workmanship in the shaping and mounting of the lenses, and partly to chromatic and spherical aberration, which increase with the aperture. As a result of these imperfections, the image of a point, instead of being a point, is a round spot called a *circle of aberration*. If  $k$  be the angular diameter of this circle for a point on the axis as it would be seen from the distance  $l$ , and  $\zeta$  the angular diameter to which it is amplified by the eyepiece, we have

$$\zeta = k \frac{t}{f_2}.$$

$k$  is called the *aberration-constant* of the objective.

**36. The Critical Amplification.** The smallness of the aberration-constant measures the goodness of performance of the objective; but in practice it is more convenient to use another quantity, which is inversely proportional to the aberration-constant and can be more easily observed, namely, the *critical amplification*, that is to say, the highest amplification that the image formed by the objective can bear without perceptible loss of sharpness. As amplification is increased, the angular diameter  $\zeta$  of the circles of aberration is increased; and when this diameter has become larger than the smallest magnitude distinguishable by the eye, sharpness begins to diminish.

**37. Older Achromatic Objectives.** According to Abbe's observations,<sup>1</sup> in even the best objectives of the old kinds the critical amplification for large apertures is only from 4 to 6. The optical qualities of the silicate glasses employed made it impossible to exceed this limit. On the one hand, the difference in the runs of dispersion of crown and flint gives a secondary spectrum after achromatising; and on the other, the dependence of dispersion on index makes it impossible to correct spherical aberration for more than one colour. Thus, for rays of shorter wave-length the system is generally spherically over-corrected (the focus for the central rays being shorter than for the border rays), and for rays of longer wave-length, under-corrected.

Hence it follows that, if the foci of the *C* and *F* rays are united for the central zone, the focal length will be greater for *F* than for *C* in all the other zones; thus the marginal zones will be chromatically over-corrected by amounts increasing towards the rim.

Practically spherical aberration is always corrected for the most intense rays. In the secondary spectrum of the central zone these have approximately the shortest focus; and the remaining rays are united in pairs, each more refrangible ray with one less refrangible. In these circumstances the change in the secondary spectrum in the outer zones is easily observable, the more refrangible colours being displaced in the positive, the less refrangible in the negative direction. Thus the uncompensated portion at the blue end of the spectrum grows longer as we proceed from centre to rim. This defect may be lessened by chromatically under-correcting the central zone, so as to produce union of *C* and *F* for one of the intermediate zones.

**38. Apochromatic Objectives.** It has been shown above (Art. 19) that with the new glasses it is possible to achromatise so that only a *tertiary* spectrum is left. This result is essentially dependent on the fact that the relation which exists in the silicate glasses between total dispersion and run of dispersion is got rid of by the introduction of borates and phosphates.

Further, the total dispersion is rendered largely independent of the index. Hence it is possible to correct axial spherical aberration.

<sup>1</sup> "On the Relation of Aperture and Power, etc.," *Journ. of the R. Micr. Soc.*, Ser. 2, Vol. III. p. 803 (1883).



tion for two colours. This result is most perfectly attained by combining the new glasses with flourspar.

The name *apochromatic* has been given, at Abbe's suggestion, to objectives in which the secondary spectrum is abolished, and the spherical aberration corrected for two colours. Their superiority to the old achromatic objectives may be gathered from the fact that, even for the largest apertures, their critical magnification amounts to at least 12—15. For medium and small apertures it is considerably greater.

**Relieving the Objective.** This improvement in quality lessens the necessity for high power in the objective; for a given total magnification can be obtained with a lower magnification by the objective when higher amplification is available. Thus the very short focal lengths hitherto regarded as essential are now superfluous, since even large apertures can be fully exhausted with objectives of moderate focal length.

With an ordinary achromatic, the smallness of the critical amplification prevents the full utilisation of large apertures. An apochromatic shows as much detail as an achromatic of larger aperture and shorter focal length.

**Increased Range of Magnification.** The range of serviceability of an objective extends from its own intrinsic magnification to the multiple of this determined by the critical amplification. A single apochromatic can therefore be used for both lower and higher powers than a single achromatic of the ordinary kind.

**Correction of the Chromatic Difference of Magnification.** In apochromatic objectives, as in others, the magnification is unequal for different colours; the blue and violet images being larger than the red and yellow. This difference of size could only be corrected by introducing other more serious defects. But apochromatics have a great advantage in this respect. For while in achromatics the difference varies from centre to circumference, in apochromatics it can be made approximately equal for all zones of the aperture, and can therefore be corrected by a suitable eyepiece.

For this purpose, it is only necessary to assign to the eyepiece an equal difference but of opposite sign. As it is convenient to be able to use the same ocular with various objectives, objectives should all be made with the same chromatic difference, even



including those of small apertures, in which the difference could easily be made non-existent.

**Order of Ray-Union.** In dioptric language the ray union effected by a simple lens is said to be only of the 1<sup>st</sup> order, since two rays proceeding from a point on the axis will not exactly meet again on the axis, if they have different refrangibilities or different inclinations to the axis. In apochromatic objectives the achromatism attained raises the ray union to the 3<sup>rd</sup> order. It is further raised by the spherical correction employed with larger apertures, to the 10<sup>th</sup> order, and finally, by equalisation of chromatic differences of magnification for different zones, to the 11<sup>th</sup> order. The diameter of the clear aperture of the objective is thus raised to 2·8 times the focal length.

**Bearing on Microphotography.** The most intense visual image of an object is produced by rays from near the red end of the spectrum, and the most intense photographic image by rays from near the violet end. An imperfect achromatism which leaves a noticeable difference of focal length between these two classes of rays makes the two images fall in different planes. Hence the focussing of the photographic image is uncertain, and cannot be verified by eye observation. Again, if the spherical correction only extends to the brightest part of the spectrum, the photographic image will be lacking in sharpness as compared with the visual one. Apochromatic objectives have in these respects an immense advantage for microphotography. By their aid alone can we secure that the photographic and visual pictures shall be in the same plane, and both equally sharp.

With the introduction of apochromatics, the theoretical advantage of microphotography over eye observation was first realised in practice. As the wave-length of the rays which are most active chemically is only  $\frac{3}{4}$  of the wave-length of those which most affect the eye, the resolving power of an objective when used photographically should (by equation (2), Art. 32), be  $\frac{4}{3}$  of its resolving power for direct vision. The advantage of microphotography over direct vision should therefore be equivalent to multiplying the aperture of the objective by  $\frac{4}{3}$ .

The essential points to be kept in view in perfecting the microscope were explicitly laid down by Abbe as far back as the year 1878; and he concluded with the following statement of aims that might be realised.

"Theory may, by going deeper into the dioptric problem, devise in course of time new methods, more effectual than those now employed for getting rid of chromatic and spherical aberration; optical workmanship may, by the introduction of improved methods and appliances, render possible a closer approximation to the mathematically exact forms theoretically required; and the allied industry of glass-making may possibly in the future produce, in place of the glasses now employed, new materials which will furnish, by their optical properties, more favourable conditions for the production of perfect systems of lenses than our present crown and flint."<sup>1</sup>

Eight years later, in July, 1886, Abbe was able to announce that these aims had been completely realised.<sup>2</sup> A set of apochromatic objectives and compensating eyepieces had been completed, in accordance with his calculations, in the optical factory of C. Zeiss, from new glasses made at the Jena Works.

**39. Use of Fluorspar for Apochromatic Objectives.** On this subject—briefly mentioned above—Abbe has published detailed information of great interest.<sup>3</sup> The chief results are embodied in the following table, which includes three glasses for comparison. The symbols have the same meaning as in preceding tables. (See Art. 17.)

	$n_D$	$10^5 \Delta$	$\nu$	$10^5 \delta_3$
				$10^3 \gamma$
Fluorspar, - - - -	1.4338	455	95.4	255 561
Lime Silicate Cr. O. 60, -	1.5179	860	60.2	487 566
Light Phosphate Cr. O. 225, -	1.5159	737	70.0	407 552
Borate Flint O. 252, - -	1.5521	1026	53.8	582 567

<sup>1</sup> "Die optischen Hilfsmittel der Mikroskopie." *Bericht über die Wissensch. Apparate auf der Londoner Internat. Ausstellung in 1876*, I. 420 (Brunswick, 1878).

<sup>2</sup> "Ueber Verbesserungen d. Mikroskops." *Sitzungsber. d. med.-natur. Ges. Jena*, 1886.

<sup>3</sup> *Zeitschr. f. Instrumentenk.*, 10, 1 (1890).

It will be seen that the index of fluorite is very small compared to that of the glasses. Now the conditions for the correction of spherical aberration in a compound objective require that two media which have a common surface of contact should have a considerable difference of index. Suppose that an ordinary crown of index 1.52 is to form one component of a cemented doublet, and that the difference of index required for removal of spherical aberration is 0.20; then for the other component a flint of index 1.72 must be used, *i.e.* a glass of excessive density and dispersion. But if fluorite is substituted for the crown glass, then a flint of index 1.63 will suffice, and this is in many ways a great advantage. The advantage is especially great for the construction of microscope objectives of large aperture.

Further, the dispersive properties of fluorspar are remarkably favourable for achromatism.<sup>1</sup> Its  $\nu$  is 95.4, whereas the highest  $\nu$  for any glass is 70.0 for light phosphate crown. Its  $\gamma$  is, nevertheless, considerably greater than that of the phosphate. Hence the secondary spectrum can be got rid of by the aid of fluorite, and, for combination with a given flint glass, less curvature in the surfaces will be required with fluorite than with crown.

So far as achromatism alone is concerned, spherical aberration being left out of account, a combination of fluorite with crown O. 60 would give an almost perfect colour-union, in consequence of the very large difference in  $\nu$  and the very slight difference in  $\gamma$ .

These considerations naturally suggested the attempt to obtain some of these benefits by employing fluorspar as an ingredient in glass. Indeed, Schott had already,<sup>2</sup> at an early stage of his researches, succeeded in producing glasses containing fluor, which showed small index and greatly diminished dispersion. But this was only on a very small scale; and the experiments showed that the difficulties in the way of obtaining homogeneous meltings were exceedingly great.

Abbe therefore introduced lenses of fluorspar itself into microscope objectives. In 1884, at Zeiss' works, various objectives containing one, two, or three fluorspar lenses instead of crown were made from his calculations. When apochromatic lenses were introduced, the mineral was brought into regular use at Jena in conjunction with the new glasses, and the example was soon

<sup>1</sup> See Art. 18.

<sup>2</sup> See Art. 6.

followed by other opticians. The result is a lessening of labour both in calculation and practice; for without fluor it would have been necessary to make the lens systems even more complicated and difficult to construct than they are at present.

Abbe has published interesting information respecting the difficulty of obtaining a suitable supply of the mineral—a subject to which it is desirable to direct attention.<sup>1</sup> The only place (on the Schwarzhornstock in the Bernese Oberland,) which in the past has furnished large clear pieces, is quite worked out. At present it is necessary to be content with comparatively small pieces, and even these can only be obtained by laborious selection.

**40. Zeiss' Sets of Apochromatic Objectives and Compensating Eyepieces**<sup>2</sup> have the properties described in Art. 38. The following is a list of the objectives:

	Numerical Aperture	Focal Length	Magnification
Dry System,	0.30	24.0 mm.	10.5
		16.0	15.5
	0.60	12.0	21
		8.0	31
	0.95	6.0	42
		4.0	63
Water Immersion,	1.25	2.5	100
Homogeneous Immersion,	1.30	3.0	83
		2.0	125
	1.40	3.0	83
		2.0	125

They are constructed to suit either the short (Continental) tube of 180 mm. or the long (English) of 270 mm. optical length, except those of focal lengths 24, 12, and 6 mm., which are not suitable for the short tube. The 2 mm. objectives for homogeneous immersion are supplied "in compliance with desires for the highest possible magnifying power of objective," although the

<sup>1</sup> *Ibid.*, 5-6.

<sup>2</sup> *New Microscope Objectives and Eyepieces by Zeiss, made of special glasses from the Jena Laboratory. Jena, 1887.*



apertures are fully utilised by the 3 mm. objectives. Every detail of the construction is carried out in strict accordance with previous calculation, all empirical modifications being excluded. The magnifications specified in the last column are for unit amplification.

The following is a list of the **Compensating Eyepieces**, showing their focal lengths, and the amplifications which they give when used with the indicated tube lengths:

	Tube	For finding		For working				
		1	2	4	8	12	18	27
Amplification, -	—	1	2	4	8	12	18	27
Focus in mm., -	Short,	180	90	45	22.5	15	10	—
Do., -	Long,	—	135	67	34	22.5	15	10

These eyepieces embody an essentially new optical construction. The high amplifications here specified could not be obtained with the Huygenian or other older constructions, without making the eye lens too small, and the eye point too close to it.

**Trials on Test Objects** were undertaken by Dippel<sup>1</sup> and Schulze.<sup>2</sup> Dippel, using a short tube, observed the following: With the 16 mm. objective:—Sections of Echinometra, sections of wood stained in two colours, the starch grains of potato-berries, laminated and spirally streaked cell walls, splitting up of nuclei, and transversely striated muscular fibre. With the 4 mm. objective:—Nitzschia sigma, Grammatophora oceanica, Surirella Gemma, Pleurosigma angulatum, Nitzschia vermicularis (the transverse striation being distinctly visible with oblique illumination), layers of thickening in cell walls of plants, tubercle bacilli. With water immersion:—Nitzschia Sigmoidea, Amphipleura pellucida (the finest transverse striation being plainly visible with oblique illumination). With homogeneous immersion:—Navicula rhomboides, the markings on the scales of Surirella Gemma, the strings of pearls on the scales of Amphipleura pellucida (with oblique illumination). In every instance the actual resolving power reached the theoretical standard, and the sharpness of the images and their purity of tint were remarkable. The strongest dry system gave as good results as can be obtained

<sup>1</sup> Zeitschr. f. wissenschaft. Mikr. u. mikr. Techn., 3, 303 (1886).

<sup>2</sup> Phil. Soc. of Glasgow, 17, Nov. 1886.

by water immersion with the old achromatics; and water immersion gave as good as the old homogeneous immersion.

Schulze, who tested the objectives of 16, 4, 2.5, and 2 mm. focus, gave the following verdict: "They surpass by far any objective I have previously examined. Their definition is exquisite, their resolving power is very great, and the pictures yielded by them are most brilliant and free from colour; they possess, further, a very notable increase of illuminating power and give great flatness of field."

**41. Monobromonaphthalin Immersion.** Equation (1) of Art. 32 shows that, in an immersion system, the index of the intervening medium must be greater than the required numerical aperture. The same rule applies to the indices of the front lens and of the cover-glass. N.A. 1.40 is attained with a fluid of index 1.52 (cedar oil). Monobromonaphthalin, with index 1.66, therefore suggested itself as a suitable medium for an attempt at a higher result; and by its aid the limit of N.A. was increased to 1.60.<sup>1</sup> For cover-glass and front lens, a flint glass of index 1.72, a special melting, was employed. Abbe's calculations showed that, in the new objective, spherical and chromatic aberration could be corrected almost as completely as in the apochromatics. The focal length given it was 2.5 mm., which makes the intrinsic magnification 100. Special cover-glasses must be ground and polished to correspond.

If it be intended to observe with very oblique illumination, or with an illuminating beam of very wide angle, the front lens of the condenser, and the object holder, must also be of strongly refracting flint glass, and the space between them must be filled with monobromonaphthalin.

The necessary test objects were prepared by van Heurck (of Antwerp), who obtained the first specimen of the new objective and employed it for the study of diatoms.<sup>2</sup>

No immersion fluid suitable for further increase of aperture is at present known.

**42. Projection Eyepieces.** Abbe has introduced a new construction, by which the advantages of apochromatic objectives

<sup>1</sup> S. Czapski, *Zeitschr. f. wissensch. Mikr. u. f. mikr. Technik.*, 6, p. 417 (1889).

<sup>2</sup> *La nouvelle combinaison optique de M. M. Zeiss et la structure de la valve des diatomées.* Dr. H. van Heurck, Anvers, 1890.

are rendered available for purposes of projection.<sup>1</sup> The objective forms its image in the same way, and at the same point of the tube, as for eye observation, and a special combination of lenses throws a projection of this image on the photographic plate or on a screen. As this combination has the appearance of an eyepiece and is inserted in the tube in the same way, it is called a projection eyepiece. It is exactly corrected for spherical and chromatic aberration, and is arranged to compensate like an ordinary eyepiece for the chromatic difference of magnification.

The linear magnification of the projected image is easily calculated. When the projection eyepiece is used with the microscope, the upper focus of the whole system is shifted into coincidence with the end plane of the eyepiece. By the general law of lens systems, the magnification is equal to the distance  $F'Q$  of the image from this plane divided by the focal length  $f'$  of the system. Let  $\phi$  denote the focal length of the objective; then the magnification  $m$  may be expressed as

$$m = \frac{F'Q}{\phi} \cdot \frac{\phi}{f'}$$

$F'Q$  is to be directly measured,  $\phi$  is assumed to be known, and the value of  $\frac{\phi}{f'}$  (called the *amplification* in the case of projection eyepieces,) is got from the number of the projection eyepiece.

Zeiss' projection eyepieces Nos. 2 and 4 are intended for the short tube, Nos. 3 and 6 for the long tube. The two lower powers are meant for giving objective demonstrations of microscopic objects, and for photographing on a small scale or with the plate at a considerable distance; the two higher powers are for photographing with a short camera.<sup>2</sup>

**43. Projection Objectives** of 75, 70, and 35 mm. focus, to be used directly, without the aid of a projection eyepiece, have been constructed by Zeiss for depicting large objects. They have very low magnification and as large a field of view as possible.<sup>3</sup>

<sup>1</sup> For an account of the older methods and their drawbacks see Zeiss' *Special Catalogue of Apparatus for Microphotography*, Jena, 1888, p. 32.

<sup>2</sup> Directions for using the projection eyepieces, together with specimens of their performance, are given in the *Special Catalogue*.

<sup>3</sup> *Ibid.*, p. 27.

**44. Semi-apochromatics.** We apply this name to the objectives constructed by various makers from Jena glasses without the use of fluorite. They far surpass ordinary achromatics without attaining the full excellence of apochromatics.

The following series of semi-apochromatics are made by Reichert of Vienna<sup>1</sup> from phosphate and silicate glasses:

	Aperture	Focus
Homogeneous Immersion	1.20—1.25	1.8 mm.
		1.3
	1.30—1.35	1.8 1.3
	1.40—1.43	1.8

One of these objectives, with aperture 1.24 and focus 1.8 mm., was tested by Nelson,<sup>2</sup> who reports, "This lens is the finest oil-immersion I have ever seen excepting only the apochromatics."

The "pantachromatic" objectives by Leitz of Wetzlar,<sup>3</sup> with which Huygenian eyepieces can be used, are graded as follows:

	Aperture	Focus
Dry System	0.12	34 mm.
	0.32	15
	0.75	7
	0.87	3.5
Homogeneous Immersion,	1.30	2.5

The semi-apochromatic made by Korista<sup>4</sup> of Milan is an oil-immersion objective of N.A. 1.30 and focus 1.7 mm.

Under the designation, "Apochromatic Objectives without Fluorspar," Meyer & Co.<sup>5</sup> of Zurich have introduced the following set:

	N.A.	Focus.
Dry System	0.31	15 mm.
	0.87	3.4
Homogeneous Immersion	1.30	2.3

<sup>1</sup> Price list, xvii. (1890).

<sup>2</sup> *Journ. of the R. Microscop. Soc.*, London, Feb. 1900.

<sup>3</sup> Price list, No. 34 (1891).

<sup>4</sup> Catalogue, 1892.

<sup>5</sup> Price List, 1893-94.



## CHAPTER IV.

### CONTINUATION OF THE SAME SUBJECT. PHOTOGRAPHIC OBJECTIVES.

45. The introduction of new kinds of glass into photographic objectives has rendered improvement possible in several directions.

In the first place, the use of glasses very free from colour has increased the luminous power of the objective, an advantage which speaks for itself.

Secondly, similarity of run of dispersion in the two components of a doublet has brought about shortening of the secondary spectrum, or even the attainment of a tertiary.

It should here be remarked that the correction of chromatic aberration on the axis of a photographic objective ought to be planned with a view to the coincidence of a sharp photographic with a sharp visual image—a purpose which requires the shortening of the secondary spectrum. On the other hand, the sharp focussing of red rays which is peculiar to the tertiary spectrum,<sup>1</sup> though important for visual purposes, is of no value for photography, and does not affect the sharpness of the photographic image, so long as the chemical action is practically confined to rays of short wave-length. This consideration suffices to show that the apochromatic correction has not the importance for photographic objectives which it has for microscopic.

A third improvement, more important than either of the foregoing, is that it has been found possible, by means of the new Jena glasses, to obtain photographic images free from astigmatism

<sup>1</sup> See Art. 19.

and at the same time free from curvature. This matter requires a somewhat elaborate explanation.

**46. Astigmatism and Curvature of Image.** Let us take as object a plane in front of the objective cutting the optic axis at right angles in a point *A*. Let *B* be the image-point corresponding to *A*. Then the plane at right angles to the axis through *B* is the ideal image-plane. But in general the objective forms, instead of a plane image, two curved image-surfaces, which touch the ideal image-plane at their common vertex *B*. In each of these two surfaces, all *points* of the object-plane are represented by short *lines*, the directions of these lines being different in the two surfaces. In one surface the lines point to the axis, and may be called radial; in the other they have the perpendicular direction, and may be called tangential. The surface with the tangential lines is called the *primary* image surface; that with the radial lines, the *secondary*. The primary surface contains sharp images of tangential lines only, the secondary of radial lines only.

Images of points of the object away from the axis are formed by means of obliquely incident pencils, whose vertical angles depend on the position and size of the opening in the diaphragm. The ray which goes through the centre of the opening is called the *principal ray* of the pencil. The plane through the principal ray and the axis of the objective is called the *meridional section*; and the plane perpendicular to this (through the principal ray) the *sagittal section*.

Rays of such a pencil, originally proceeding from a point, will not as a rule meet again in a point after refraction; thus the refracted pencil is *astigmatic*. This is due to the fact that rays in meridional and rays in sagittal planes converge with unequal rapidity. If the sagittal convergence is stronger than the meridional, the rays will first form a short radial focal line, and then, further on in their course, a tangential one.

**Testing an Objective for Astigmatism.** The most obviously suitable test object for this purpose is a target carrying a system of concentric circles with their radii. It should be so placed that the common axis of the circles coincides with the axis of the objective. If the objective is astigmatic, it will be impossible to adjust the receiving screen so that the circles and the radii are

simultaneously depicted sharp at parts of the field distant from the axis; for the circles are only pictured sharply in the primary image surface, and the radii only in the secondary. (A cross-ruled pattern of straight lines is also a suitable test.) The distance between the two positions of the screen, one of which makes the radial and the other the tangential lines sharp, *at the outer edge of the field*, is called the *astigmatic difference*.

### **Curves of Field Curvature and of Astigmatic Difference.**

To give a clear representation of the behaviour of a given objective as regards the defects in question, two curves may be drawn, taking as abscissa the angular distance of any part of the image from the axis, and as ordinates the distances of the primary and secondary images from the ideal image plane. If a third curve be drawn, having as its ordinates the differences of the ordinates of these two, it will represent the variation of astigmatic difference. Such curves have been plotted by P. Rudolph, for various objectives.<sup>1</sup>

**Defective Definition at Edge of Field.** The images formed by photographic objectives are, in practice, always thrown on plane plates perpendicular to the optic axis. If the object be also a plane perpendicular to the axis, the curvature of both images causes loss of definition at the edge, when the focus is adjusted for the centre. Even if the curvature of *one* image is got rid of, astigmatism will still cause difference in sharpness between tangential and radial lines. Equality of definition over the whole field can only be obtained by correcting both for astigmatism and curvature. This is called *anastigmatic flattening* of the image.

Since a flat object gives a curved image, conversely a flat image will be given by a certain curved object-surface, which we shall call the *conjugate surface*. Thus a sharp image can sometimes be obtained when the objective is only corrected for astigmatism, and not for curvature.

**Penetration or Focal Depth.** Suppose the object not to be flat, but to have considerable depth from front to back. Then those points of the object whose images lie in a plane will lie on the conjugate surface, which may either be curved or plane according to the nature of the objective. If the marginal portion of the lens is sufficiently stopped out by a diaphragm, points of

<sup>1</sup> *Eders Jahrb. f. Photographie*, 1891, 233, 235; 1893, 223, 224.



the object within certain limits of distance from the conjugate surface, on both sides, will also be in good focus. It is easily shown that, for a given objective, this *focal depth* increases with the distance of the object, and also (unless the conjugate surface is plane) varies with the distance from the centre of the field.

**Distortion of Image.** A large astigmatic difference may sometimes destroy the resemblance of the image to the original.<sup>1</sup> If, in the first test object mentioned above, one part, near the edge of the field of view, has its radial and tangential lines so close together as to form a fine network with square meshes, the network, if there is much astigmatic difference, will not be clearly visible in the image; the radial lines being invisible in the primary image-surface, and the tangential in the secondary; so that with one adjustment we shall see only tangential, and with another, only radial lines. A midway adjustment will usually show the network with both sets of lines blurred; and the blurring may be so great as to cause them to be invisible except where they overlap. The intersections will, in this case, be represented as squares with narrow spaces between them, suggesting a reversal of light and dark in the pattern.

If the object is rotated through  $45^\circ$ , so that the diagonals of the square meshes are radial and tangential, the squares of the original pattern are changed, in either image-surface, into narrow hexagons, having their length tangential in the primary surface and radial in the secondary. With increasing astigmatic difference the appearance more and more resembles a simple alternation of light and dark stripes.

**47. The Introduction of Phosphate Crown and Borate Flint into Photographic Objectives** has been confined to a few trials, some of them directed to anastigmatic flattening and others to the perfecting of achromatism.

**The Anastigmatic Aplanat. Normal and Anomalous Doublets.** The problem of the simultaneous removal of astigmatism and curvature—in other words, of simultaneously flattening the primary and secondary image-surfaces—was first solved, in an imperfect way, by Miethe's use of phosphate crown and borate flint.

Of previous attempts in this direction, one of the most success-

<sup>1</sup> See Rudolph, *Die Zeiss-Anastigmaten*. *Phot. Wochenblatt*, 1892. Nr. 18-21.



ful was Steinheil's aplanat. It consisted of two identical achromatic doublets, placed symmetrically on opposite sides of a diaphragm. When the two doublets were moved nearer together or further apart, the primary image-surface was more affected than the secondary. Increase of distance between the doublets rendered the primary surface flatter, and diminution of their distance diminished the astigmatic difference. Both advantages could not be attained simultaneously. This impossibility had its root in the uniform relation which connected the optical constants of all the available glasses.

An achromatic doublet is always made of two glasses which have very different values of  $\nu$ .<sup>1</sup> If the focal distance is to be positive, the glass with greater  $\nu$  is the positive component of the doublet.<sup>2</sup> For the old silicate glasses, the rule held that the glass of greater  $\nu$  had the smaller index of refraction  $n$ . An achromatic converging doublet therefore always consisted of a converging lens of crown and a diverging lens of flint, the flint having the larger index. But in order to obtain anastigmatic flattening, in conjunction with achromatism, it is necessary that the converging lens should have the greater index. This requires that the glass of greater  $\nu$  should also have the greater  $n$ . Rudolph has given the name *anomalous* to doublets constructed on this principle, those constructed on the old principle being called *normal*.<sup>3</sup> The names are also applied to pairs of glasses suitable for the formation of such doublets. Lummer, instead of *anomalous* and *normal*, uses the names *new* and *old* achromatic.<sup>4</sup>

With the glasses formerly available, it was impossible to select a pair of glasses which would form an anomalous doublet with any considerable difference between their values of  $\nu$  or of  $n$ . The introduction of highly refracting phosphate crown, however, rendered such a selection possible; and for this glass, combined with weakly refracting flint, Miethe calculated an objective, to which he gave the name of *Anastigmat*.<sup>5</sup> It consisted of a combination of two identical anomalous doublets corrected as far as

<sup>1</sup>  $\nu$  is the reciprocal of "dispersive power" defined in a definite way. See Art. 17.

<sup>2</sup> Art. 18, equation (3).

<sup>3</sup> *Brit. Jour. of Phot.*, 33, 443 (1890).

<sup>4</sup> Müller-Pouillet, 9th ed., II., 1, 762. Also S. P. Thompson's translation of Lummer's *Photographic Optics*.

<sup>5</sup> *Vogels Phot. Mitt.*, 25, 123 and 173 (1888).

possible for spherical aberration. Samples having a focal length of about 9.75 cm. were made by Hartnack at Potsdam in 1884, and showed, as regards nearness of the two image-surfaces to each other and to the ideal image plane, as much superiority over the best previously known objectives as he had expected from theory. The objection to the practical introduction of this first anastigmat objective lay in the insufficient durability of the phosphate crown employed.

**The Wide-Angled Apochromat** constructed by Fritsch<sup>1</sup> of Vienna in 1889 has been classed among aplanats. It was a normal doublet of phosphate crown and borate flint, designed not for getting rid of astigmatism, but for sharpening the chemical image, and bringing it nearer to the visual image, by shortening the secondary spectrum.

**An Apochromatic Triplet**, calculated by Rudolph on a plan suggested by Abbe, was made by Zeiss<sup>2</sup> in 1890, and for a few years after. Its construction is fundamentally the same as one recommended by H. Schröder for astrophotography,<sup>3</sup> and is chiefly intended for increasing the available aperture by more complete correction for spherical aberration. There are two simple convex lenses, and between them, but not touching them, is a compound lens of relatively long focus, consisting of two or three lenses cemented together, intended to correct the spherical and chromatic aberration. In the apochromatic objectives of this construction, the two concave components of the correcting lens were of borate flint, and the convex lens between them, as well as the two separate lenses, were made from one and the same specimen of crown. The two kinds of glass form a normal pair. The primary image-surface is flattened, and the astigmatic difference is of the same order of magnitude as in the aplanatic type.

These objectives are no longer made, as the apochromatic correction is of no great advantage, and there was special difficulty in making the glasses free from defects.

**48. Light Baryta Flints** have come into extensive use, and possess properties which are of great advantage for photographic

<sup>1</sup> *Phot. Korrespondenz von L. Schrank*, 26, 12 (1889).

<sup>2</sup> See German Patent, No. 55313, and Zeiss' Catalogue for 1891, pp. 9, 18.

<sup>3</sup> *Ast. Nachr.*, No. 2682.

objectives. The two leading types—landscape lenses and aplanats—were introduced by Voigtländer as long ago as 1888.<sup>1</sup>

The baryta glasses differ from the silicate glasses in having smaller absorption of the highly refrangible rays, and—as a result of this difference—smaller increase of dispersion with decrease of wave-length. By combining the lighter crowns with the baryta light flints, doublets can be constructed which are very transparent for both visual and chemical rays, and sufficient amounts of difference in  $\nu$  and  $n$  can be obtained without the high dispersion which was previously unavoidable. These favourable conditions have given an increase of light; and the better flattening of the primary image has permitted an enlargement of the field of view.<sup>2</sup>

**49. Baryta Crown and Silicate Crown.** With the help of highly refractive baryta crown and highly dispersive silicate crown, the problem of anastigmatic flattening was attacked afresh, and finally received several satisfactory solutions.

**Concentric Lens.** Ross of London in 1888 made an anastigmatic objective, calculated by Schröder,<sup>3</sup> which, like Miethe's nearly contemporaneous anastigmat, belonged to the aplanatic type of construction. Each of the two achromatic doublets

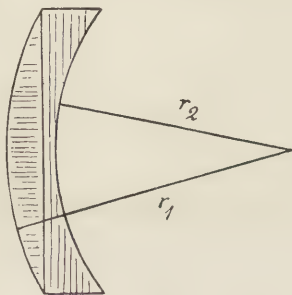


FIG. 7.

consists, as in fig. 7, of a plano-convex baryta crown and a plano-concave silicate crown lens. The objective takes its

<sup>1</sup> *Vogels Phot. Mitt.*, 25, 185 (1888); *Eders Jahrb. f. Phot.*, 1889, 100; *Phot. Mitt.*, 25, 196 (1888). This last reference gives the information that baryta flint had taken the place of borate flint in Zeiss' apochromatic triplet.

<sup>2</sup> For further particulars see "Unsymmetrical Anastigmats" in the next Art.

<sup>3</sup> English Patent, No. 5194 of 1888, published 1889. *Phot. News*, 33, 1, 316.



name from the fact that the two outer spherical surfaces are concentric. The index of the baryta crown lies between 1.50 and 1.53. The baryta has the smaller dispersion, as well as the greater index, and has consequently the greater  $\nu$ ; thus the two glasses form an "anomalous doublet." The objective consists, like Miethe's, of two doublets precisely alike.

Calling the two radii  $r_1$  and  $r_2$ , as indicated in the figure, we have, in the notation of Art. 18,  $k = 1/r_1$ ,  $k' = -1/r_2$ , and equations (3) of that Art. become

$$r_1 = d\Delta(\nu - \nu'), \quad -r_2 = d\Delta'(\nu' - \nu);$$

the accented letters referring to the plano-concave lens, and the unaccented to the plano-convex. For the focal length  $d$  of the combination, we have

$$d = \frac{r_1}{\Delta(\nu - \nu')} = \frac{r_2}{\Delta'(\nu' - \nu)},$$

and as  $\nu$  is greater than  $\nu'$ , the focal length is positive. For a normal doublet of the same form the focal length would be negative.

The objective was not placed on the market till 1892, as up to that time the glasses required were not produced with sufficient uniformity.<sup>1</sup> The construction was not in all respects an advance. It gave weak illumination; and while the margin of the image was improved by better anastigmatic correction, the centre of the field lost definition by increased spherical aberration.

**Zeiss' Unsymmetrical Anastigmats** (D.R.P. 56109). As already explained, anomalous combinations of two glasses furnish the means of constructing achromatic systems by which both image-surfaces are brought near to the ideal image plane. But this arrangement does not, like the normal arrangement, easily lend itself to the removal of spherical aberration. The first anastigmatic objectives did not meet this difficulty; although in Miethe's anastigmat the spherical aberration was inconsiderable, owing to the favourable qualities of phosphate crown.

Rudolph was the first to overcome the mutual incompatibility of these two corrections. He gave up the symmetrical construction characteristic of aplanats, and adopted an unsymmetrical

<sup>1</sup> *British Jour. of Phot.*, 39, 273 (1892) and *Eders Jahrb. f. Phot.*, 1893, 13 and 348.



arrangement,<sup>1</sup> as Steinheil had previously done with less success, in his "antiplanetic." The objective which he designed has two members, each independently achromatised, one of them being a normal pair of silicate crown and baryta light flint, and the other an anomalous pair of baryta crown and silicate crown. This plan makes it possible to compensate the spherical aberration of the second member by means of the first, and the astigmatism of the first by means of the second.<sup>2</sup> The first anastigmat of this construction was brought out in 1890 in three series;<sup>3</sup> to which, in the course of the next year, four others were added, the "relative apertures"<sup>4</sup> of the seven series being  $1/4.5$ ,  $1/6.3$ ,  $1/8$ ,  $1/7.2$ ,  $1/9$ ,  $1/12.5$ ,  $1/18$ .<sup>5</sup> The first member is always a doublet; the second is a triplet in the first three, and a doublet in the last four. Fig. 8 shows an anastigmat of the first series, of 150 mm. focal length, in  $\frac{2}{3}$  actual size. It has an angle of about  $75^\circ$  and gives a very bright image. Fig. 9 is an objective of the seventh series, of 632 mm. focus, shown  $\frac{2}{3}$  actual size.

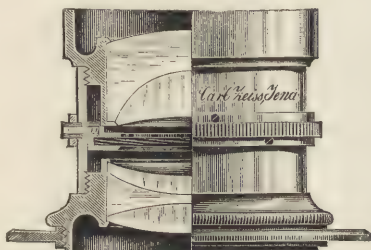


FIG. 8.

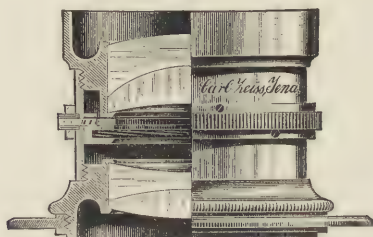


FIG. 9.

The advantages of this combination of an old achromat with a new achromat, over all former objectives, have been fully discussed by Rudolph.<sup>6</sup> They result chiefly from the previous impossibility of avoiding astigmatic curvature of images in objectives well corrected for spherical aberration (see Art. 46). Other advantages are:—the favourable position of the images formed by reflections at the boundaries of air and glass, the resulting flare

<sup>1</sup> English Patent, No. 6028. *Brit. Jour. of Phot.*, 33, 443 (1890).

<sup>2</sup> *Eders Jahrb. f. Phot.*, 1891, 225, and 1893, 222.

<sup>3</sup> *Vogels Phot. Mitt.*, 27, 84 (1890).

<sup>4</sup> Relative aperture is diameter of objective divided by focal length.

<sup>5</sup> Zeiss' list of photo-objectives, 1894.

<sup>6</sup> *Eders Jahrb. l.c. and Phot. Wochenblatt*, 1892, Nos. 18-21.

being thus reduced to a minimum; the increase in light due to freedom of the glass from colour; and the short distance between the two members of the objective, which, together with the anastigmatic flattening, tends to prevent rapid falling off in brightness at the margin.

**Anastigmatic Compound Lens.** The principle of mutual correction of two doublets adopted in the unsymmetrical anastigmats has also been employed by Rudolph in the construction of anastigmatic single objectives composed of three lenses *A*, *B*, *C* cemented together, the two outer ones *A*, *C* being positive, and the inner one *B* negative.<sup>1</sup> If the spherical correction is assigned to the pair *A*, *B* and the astigmatic correction to the pair *B*, *C*, while the chromatic correction is shared by all three, then the indices must increase in the order *A*, *B*, *C*, and *B* must have the smallest  $\nu$ . *B* and *C* must be an anomalous pair. The conditions can be satisfied by making *A* a silicate crown, *B* a light baryta flint, and *C* a heavy baryta crown.

The earliest of these anastigmatic triplets were made by Zeiss<sup>2</sup> in 1891, but the completion of the series was delayed, and the series was first issued in 1893. It includes 9 different focal lengths, the relative aperture being  $1/14.5$ .

**Compound Anastigmats.** Any two anastigmatic lenses, symmetrically placed so as to form a double objective, form what is called a compound anastigmat.<sup>3</sup> The useful relative aperture of such an objective lies between  $1/8.5$  and  $1/6.9$ .

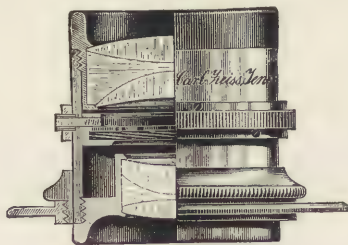


FIG. 10.

Fig. 10 represents, about  $\frac{3}{4}$  natural size, a compound anastigmat with front lens of 385 mm. focus and back lens of 250 mm.

<sup>1</sup> English Patent, No. 4692, *British Jour. Phot.*, 40, 331 (1893).

<sup>2</sup> Price List of Photogr. Objectives, 2nd supplement, 1893, and List, 1894.

<sup>3</sup> Zeiss' Catalogue, 1893, p. 8, and 1894, p. 24.

The applications of Zeiss' various anastigmatic objectives to photographic purposes of various kinds have been described by Rudolph.<sup>1</sup>

**Goerz' Double Anastigmat.** E. von Hoegh, independently of Rudolph, hit upon the principle on which anastigmatic lenses are based, and made a symmetric combination of two exactly similar triple lenses, each having one negative and two positive components.<sup>2</sup> It was accordingly designated a double-anastigmat. The first objective of this kind was made at Goerz' works in Berlin in 1892; and two series, with effective apertures  $1/7.7$  and  $1/11$ , were issued in 1893. An account of the performance of these objectives has been published by the inventor.<sup>3</sup>

**Voigtländer's Collinear.** The manifold adaptability of the new glasses in photographic optics is illustrated by the fact that Kaempfer succeeded in attaining anastigmatic flattening by a different method.<sup>4</sup> The objective designed by him also consists of two similar members symmetrically placed. Each member consists of three lenses cemented together, two of them being positive and one negative; but the negative lens, instead of being in the middle, is next the diaphragm. The principle of mutual correction of a normal and anomalous pair is not employed. In each member the middle lens has the smallest index and is concavo-convex. Convergence is accordingly produced at one of the two cemented surfaces, and divergence at the other. Anastigmatic flattening is thus rendered possible, just as, in the systems of Rudolph and van Hoegh, astigmatic compensation between an old and a new achromatic is attained by giving the former a diverging, and the latter a converging surface of junction.

Objectives of this kind, with effective aperture  $1/6.3$ , were made in 1894 by Voigtländer of Brunswick, who gave them the name of *collinear*, because "the images which they give agree very exactly with the object itself, and thus fulfil the conditions of ideal collinear representation."<sup>5</sup> By a happy accident the collinear objective also gives achromatic union of three colours,

<sup>1</sup> *Phot. Korrespond. von L. Schrank*, 1893, No. 398, p. 512.

<sup>2</sup> English Patent, No. 23378; *Brit. Jour. Phot.*, 40, 485 (1893).

<sup>3</sup> *Vogels Phot. Mitteil.*, 30, 485 (1893-94).

<sup>4</sup> *Phot. Korresp. von L. Schrank*, 31, 455 (1894).

<sup>5</sup> *Vogels Phot. Mitteil.*, 31, 215 (1894-95).



and thus has no secondary spectrum. A patent for substantially the same construction was applied for by Steinheil of Munich in 1893.

**Zeiss' Anastigmatic Lenses.** The principle of correction used in unsymmetrical anastigmats has also been applied by Rudolph to single objectives composed of four lenses cemented together. Two doublets, each consisting of a positive and a negative lens, are united. In one doublet the greater index is assigned to the positive, and in the other to the negative lens, thus rendering anastigmatic and spherical correction compatible. As regards chromatic aberration, the two doublets can either be corrected independently or by mutual compensation.<sup>1</sup>

Since 1895 objectives of this design, with aperture  $1/12.5$ , have been made by Zeiss under the name of "Anastigmatic Lenses."<sup>2</sup> As there are a larger number of disposable elements than in triplet objectives, a more complete correction of the various errors can be attained.

An anastigmatic lens of 350 mm. focus is shown in fig. 11, on about  $\frac{3}{4}$  scale. It gives a bright image, and the angle of field is more than  $85^\circ$ .

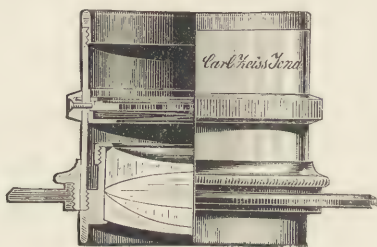


FIG. 11.

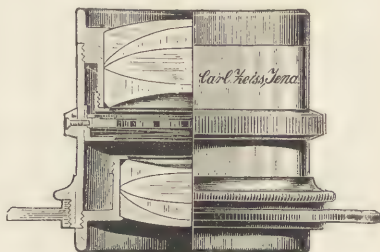


FIG. 12.

By combining anastigmatic lenses in pairs separated by an interval, as in fig. 12, a series of double objectives (compound anastigmats) is formed of effective aperture up to  $1/6.3$ . They give bright images, and the anastigmatic flattening of the field extends to wide angles.<sup>3</sup>

<sup>1</sup> English Patent, No. 19509; *Brit. Jour. Phot.*, 41, 829 (1894).

<sup>2</sup> Price List of Photog. Obj. Suppl., Feb. 1895.

<sup>3</sup> For the practical applications of this series of objectives, see Catalogue; also *Vogels Phot. Mitteil.*, 31, 355 (1894-95).



**Orthostigmatics.** The objectives recently issued by C. A. Steinheil & Sons under this name belong to the same type as Voigtländer's collinear. They are objectives with two members, each member being a triplet in which the middle lens has the smallest index.<sup>1</sup>

**50. Zeiss' Spherically and Chromatically Corrected Objective.**<sup>2</sup> The simultaneous correction of chromatic and spherical aberration presents no difficulty in a cemented doublet composed of a positive crown lens  $L$  and a negative flint lens  $L'$ , so long as the relative aperture does not exceed a certain moderate amount, about  $1/6$ . If, however, a considerably larger aperture is required, serious difficulty is encountered, arising from the connection between index and dispersion—a connection which, though rendered less stringent by the introduction of the new glasses, is not altogether abolished.

When two chromatic foci are united, let the increments of the indices  $n, n'$  from the first colour to the second be  $\delta, \delta'$ . Then, by equations (1), (2) of Art. 18, we have

$$\phi = k(n-1) + k'(n'-1); \dots\dots\dots (1)$$

$$0 = k\delta + k'\delta'. \dots\dots\dots (2)$$

These give

$$\begin{aligned} \phi\delta' &= k\{(n-1)\delta' - (n'-1)\delta\}; \\ -\phi\delta &= k'\{(n-1)\delta' - (n'-1)\delta\}; \end{aligned}$$

whence

$$k + k' = \phi \frac{\delta' - \delta}{(n-1)\delta' - (n'-1)\delta} = \frac{\phi}{n-1 - \frac{n'-n}{\delta'-\delta}\delta} \dots\dots\dots (3)$$

$k + k'$ , in the case of a cemented lens, is the sum of the two external

<sup>1</sup> See *Brit. Jour. Phot.*, 1896, 489. An outline, from the theoretical point of view, of the gradual development of the photographic objective is given by Lummer in an article entitled "Contributions to Photographic Optics," *Zeitschr. f. Instrum.*, 17, 203 (1897). See also Müller-Pouillet, *Lehr. d. Physik*, ninth edition, II. 1, 745-785, and S. P. Thompson's Translation of *Lummer's Photographic Optics*, Macmillan, 1900.

<sup>2</sup> German Patent, No. 88889 (1896).

curvatures, regarded as positive when convex; and the last expression for it shows what relations, between the constants of the two glasses, tend to keep it small, and so to diminish the positive aberration which will arise from the refractions at the two external surfaces. The external curvature will be diminished by diminishing  $n' - n$  and by increasing  $\delta' - \delta$ .

For the case  $n' - n = 0$  the external curvature is a minimum, and has the same value as for a single lens of the same focal length. In this case, the positive aberration at the external surfaces could not be compensated by a negative aberration at the surface of junction; for the rays would pass through this surface without deviation.

From these considerations, it follows that glasses would be required in which the dispersion of the flint was considerably greater than that of the crown, but its refractive power only so much greater as is sufficient for permitting compensation between the external and internal spherical aberration.

In the old optical glasses, a large value of the dispersion ratio  $\delta'/\delta$  is always associated with a relatively large value of  $n' - n$ . Hence, in achromatic doublets of large aperture, the external curvature is always unfavourable for the correction of spherical aberration.

**Introduction of Hyperchromatic Diverging Lens.** There are two ways of overcoming this difficulty. The convex element of the objective may be replaced by a hypochromatic converging lens (Art. 22), or the concave element by a hyperchromatic diverging lens. In the former case, instead of  $\delta$ , we shall have a resultant dispersion which we can make as small as we please; in the latter, instead of  $\delta'$ , we shall have increased resultant dispersion. In both cases we can avoid undesirably large values of  $n' - n$ .

In the "spherically and chromatically corrected objective," the second course is adopted, the simple lens  $L'$  being replaced by a hyperchromatic diverging lens; with the resulting advantage that the chromatic difference of spherical aberration is less than for a simple lens of the same dispersion. This lens being cemented to the simple convex lens  $L$ , we have a triple achromatic system, which not only, by its small external curvature, renders the correction of spherical aberration easy, but also gives less over-correction in the upper portion of the spectrum than an ordinary

two-lens system, equivalent to it as regards focal length and secondary spectrum.

The hyperchromatic diverging lens can, if desired, have two convex single lenses cemented to it instead of only one.

The construction above described involves an additional lens, but this disadvantage is accompanied by several advantages. At the cemented surface inside the hyperchromatic lens there is only very slight bending of the rays. The curvature of this surface can therefore be made large without injurious consequences. Again, imperfections in the shaping of the two lens-faces which are united at this surface are almost harmless, if a cement be used having nearly the same index as the glasses—a condition easily fulfilled.

Pairs of glasses suitable for the hyperchromatic lens are available, in sufficient variety to give a good choice, for values of  $n$  ranging from about 1.54 to about 1.61.

In the specification of the patent for this construction, the following numerical data are given for two objectives actually constructed, in which the relative aperture amounts to  $1/3$ .

The first consists of three lenses  $L_1, L_2, L_3$ ; the second of four,  $L_1, L_2, L_3, L_4$ . In both combinations  $L_1$  and  $L_2$  compose the hyperchromatic diverging lens, its external curvature being denoted by  $k_e$ , and that of its convex component  $L_1$  by  $k$ . The resultant dispersion is denoted by  $\rho$ , and the unit of length employed is the focal length of the combination. The convention as to sign, for the radii of curvature  $r_1, r_2, \dots$  of the successive faces, is that  $r$  is positive for surfaces convex towards the incident light.

#### TRIPLE OBJECTIVE.

	$L_1$	$L_2$	$L_3$
$n_D$	1.60844	1.60841	1.55540
$n_G$	1.62217	1.62967	1.57036
$n_G - n_D$	.01373	.02126	
$r_1$	+ 0.4745		
$r_2$	$\infty$		
		$\frac{k}{k_e} = -0.85$	
$r_3$	+ 0.2175		
$r_4$	+ 9.8865	$\rho = 0.02763$	

## QUADRUPLÉ OBJECTIVE.

$L_1$ and $L_4$	$L_2$	$L_3$
$n_D = 1.60844$	$1.60284$	$1.51914$
$n_G = 1.62217$	$1.62060$	$1.53020$
$n_G - n_D = .01373$	$.01776$	
$r_1 = +0.492$		
$r_2 = -0.795$	$\frac{k}{k_e} = -1.65$	
$r_3 = +0.248$		
$r_4 = +0.475$	$\rho = 0.02441$	
$r_5 = +5.634$		

**51. Zeiss' Spherically and Chromatically Corrected Anastigmat.**<sup>1</sup> An objective giving strong illumination and combining good anastigmatic flattening over a large field with specially good spherical and chromatic correction, has been constructed on the following principles.

An objective composed of two lenses,  $L$  convex and  $L'$  concave, not in contact, has four disposable radii of curvature, whence it is possible—as in Gauss' telescopic objective—to correct spherical aberration for two colours, and thus abolish chromatic difference of spherical aberration. In applying this construction to photographic objectives, the achromatising must extend to the rays most active in photography, and the anastigmatic flattening must be much more complete than is necessary in the case of astronomical objectives.

To satisfy these conditions as regards achromatism, for a large aperture, without unduly increasing the thickness of the lenses or their distance apart, it would be necessary, if our choice were confined to the old glasses, to use a very heavy flint glass for the concave lens  $L'$ , and this (see Art. 47) would be altogether incompatible with anastigmatic flattening.

The difficulty can be avoided by using a hypochromatic converging lens in place of  $L$ , or a hyperchromatic diverging lens in place of  $L'$ , or both at once.<sup>2</sup> It is not necessary that the glasses used should have exactly the same index. A difference of a few units in the third decimal place may even be advantageous, by affording opportunity for diminishing spherical aberration.

<sup>1</sup> German Patent, No. 92313 (1897).

<sup>2</sup> See Art. 22.



The patent specification gives the following particulars of two objectives, the first consisting of three lenses with a diaphragm in front, and the second being a double objective, with its two members symmetrically placed before and behind a diaphragm in the middle. The second objective has the advantage of being free from coma and from orthoscopic distortion.

Of the three lenses  $L_1, L_2, L_3$  which compose the first,  $L_1$  is a simple diverging lens, and  $L_2, L_3$  form a hypochromatic doublet,  $L_2$  being concave and  $L_3$  convex.

Of the three lenses  $L_1, L_2, L_3$  which compose either member of the second objective,  $L_3$ , which is furthest from the diaphragm, is a simple convex lens, and  $L_1, L_2$  form a hyperchromatic diverging doublet,  $L_1$  being concave and  $L_2$  convex.

To assist the memory, the single lens is in each case distinguished by square brackets. The notation is the same as in the specification of the previous article.

FIRST OBJECTIVE. RELATIVE APERTURE 1/9.

$[L_1]$	$L_2$	$L_3$
$n_D = 1.57210$	1.51158	1.51111
$n_{G'} = 1.58997$	1.52344	1.52127
$n_{G'} - n_D = .01787$	.01186	.01016
$r_1 = -0.1164$		
$r_2 = -0.2215$	$\frac{k}{k_e} = +1.85$	
$r_3 = -1.6097$		
$r_4 = +0.2708$	$\rho = 0.00871$	
$r_5 = -0.1760$		

SECOND OBJECTIVE (DOUBLE). RELATIVE APERTURE 1/4.

$L_1$	$L_2$ and $[L_3]$
$n_D = 1.57631$	1.57244
$n_{G'} = 1.59227$	1.58512
$n_{G'} - n_D = .01596$	.01268
$r_1 = -0.1954$	
$r_2 = +0.4370$	$\frac{k}{k_e} = -2.17$
$r_3 = -0.3599$	
$r_4 = -1.5424$	$\rho = 0.02306$
$r_5 = -0.3147$	

## CHAPTER V.

### CONTINUATION OF THE SAME SUBJECT.

**52. Achromatic Diverging Lenses.** Optical systems of the type of the Galilean telescope and the telephotographic objective consist of two members, one positive and the other negative. Each is separately achromatised and is usually separately corrected for spherical aberration.

In the case of the second or negative member, the simplest construction is to make it consist of two single lenses cemented together, the negative lens having the larger  $\nu$  and the smaller  $n$ . The achromatising depends on the differences of  $\nu$ , and the spherical correction on the differences of  $n$ . The old silicate glasses were capable of satisfying to some extent the requirements of this construction, inasmuch as  $\nu$  decreased when  $n$  increased.

This mode of constructing diverging lenses had, however, the inconvenience of giving too large curvatures to the outer surfaces. To show this, we have, by equations (3) of Art. 18,

$$k + k' = \frac{1}{d} \cdot \frac{1}{\nu - \nu'} \left( \frac{1}{\Delta} - \frac{1}{\Delta'} \right).$$

Let  $R$  denote  $\frac{1}{\nu - \nu'} \left( \frac{1}{\Delta} - \frac{1}{\Delta'} \right)$ , or  $\frac{1}{\nu - \nu'} \left( \frac{\nu}{n - 1} - \frac{\nu'}{n' - 1} \right)$ ,

so that we have

$$k + k' = \frac{R}{d} \dots\dots\dots(4)$$

For doublets of the old glasses, the smallest value that  $R$  can

have is about 2.4, and this makes the external curvature  $k + k'$  considerable when the focal length  $d$  is small. The conditions are therefore unfavourable for the removal of spherical aberration.

**53. Compound Diverging Lenses with Diminished External Curvature.** If spherical aberration is to be treated as unimportant, the constant  $R$  can be diminished by diminishing the

difference  $n' - n$ . For if we identify  $\frac{1}{d}$  with  $\phi$  in the equations of Art. 50, we have

$$k + k' = R\phi,$$

and

$$\frac{1}{R} = \frac{\phi}{k + k'} = n - 1 - \frac{n' - n}{\delta' - \delta} \delta,$$

showing that  $1/R$  is increased by diminishing  $n' - n$ . By using the new optical glasses, it is easy to obtain in this way values of  $R$  less than 2. By using anomalous doublets<sup>1</sup> in which  $\nu$  and  $n$  are greater than  $\nu'$  and  $n'$ , and  $\frac{n' - n}{\delta' - \delta}$  is negative, it is possible to reduce  $R$  below the value 1. The external curvature of the doublet diminishes with  $R$  in direct proportion.

If  $n'$  is a little greater than  $n$ , a little positive aberration will remain at the interior cemented surface. When  $n$  and  $n'$  are equal, this internal aberration vanishes completely, and the external curvature of the doublet becomes equal to that of a simple lens of the same focal length. Finally, when  $n$  is a little greater than  $n'$ , the internal aberration is negative, like that of a single diverging lens. In all three cases, taking the action at the external surfaces into account, the achromatic diverging lens will exhibit some small degree of negative aberration. This can be easily compensated by leaving in the objective a small remnant of positive aberration.

These considerations led Rudolph to a new construction for achromatic diverging lenses.<sup>2</sup> Equal or nearly equal indices are assigned to the two components of the cemented system, and the system is not spherically corrected. This gives smaller external curvature, for a specified focal length, than would be required by previous methods.

<sup>1</sup> See Art. 47.

<sup>2</sup> English patent, No. 10000. *Brit. Jour. Phot.*, 40, 659 (1893). D.R.P. 71473.

Another advantage is, that the internal aberration (at the cemented surface) is diminished; and if it is rendered negative, this facilitates correction outside the axis.

The foregoing discussion shows that baryta crown of high index is pre-eminently suitable for the negative lens of the diverging doublet, and strongly dispersive silicate crown for the positive lens. Several other pairs can, however, be selected which are sufficient for the end proposed.

Zeiss makes these achromatic diverging lenses for teleobjectives, with the four focal lengths 30, 40, 58, and 75 mm.<sup>1</sup>

<sup>1</sup> Price List of Phot. Obj., 1894, p. 30.



## CHAPTER VI.

### CONTINUATION OF THE SAME SUBJECT. TELESCOPES.

**54. Hand Telescopes with Inverting Prisms.** Of the two ordinary constructions for erect-image telescopes, known as the Galilean and the Terrestrial, the former is suitable for magnifications not exceeding 4 diameters, is simple in construction, is short, and gives a bright field. For higher magnifications it is not well adapted, owing to the smallness of its field and the falling off of light towards the margin. The terrestrial telescope, on the other hand, has a larger field with uniform illumination, but is of complicated construction, and disproportionately long. It is seldom made with lower magnification than 12, and is usually fitted on a firm stand.

Powers of from 5 to 8, which are the most useful for many purposes, are not well provided for by either construction.

This want has been supplied by introducing, between the objective and ocular of the ordinary astronomical telescope, glass prisms which, by four successive total reflections, re-invert the inverted image formed by the objective.

Two different arrangements of prisms can be used for this purpose. The first is represented in its simplest form in fig. 13. It may be regarded as built up of four equal right-angled isosceles prisms, the two faces which contain the right angle being square. The five arrows show the course of a ray which undergoes four reflections, one at each of the hypotenusal

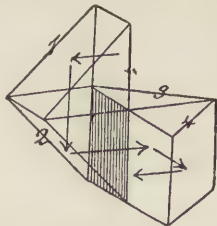


FIG. 13.

faces, and finally emerges parallel to its original direction. This system of prisms, if used alone, gives an inverted image of an object seen through it; and, when used in conjunction with an objective which of itself would give an inverted image, changes this image into an erect one.

To convert the first arrangement into the second, No. 4 prism in the figure is to be moved parallel to itself from its present position to the top of No. 3, so that its left-hand face fits against the first face of No. 1. Its two arrows are to be carried with it, and will represent the incident ray and first reflected ray, the order of succession of the prisms being now 4, 1, 2, 3, and the incident light being at right angles to its former direction.

In the first arrangement Nos. 1 and 2 may consist of a single piece of glass, and Nos. 3, 4 of another, the two pieces being cemented together at the shaded area shown in the figure. In like manner, in the second arrangement, Nos. 1 and 4 can be made in one piece, and Nos. 2, 3 in another, and the two may be cemented together.

Instead of having the four component prisms all close together, any two of them may be shifted apart, provided that the shifting is effected along the course of the ray. The prisms can also be made to do duty as lenses by giving spherical curvature to some of their faces.

**55. Collateral Advantages.** By either system of prisms, the central ray is bent four times at right angles; and as the total length of path from objective to eyepiece is a fixed quantity, the length of the telescope is thus shortened, especially if there is wide separation between the prisms. This shortening may or may not be accompanied by lateral shift of the emergent ray relative to the incident ray.

With the first system, the maximum shortening for a given amount of lateral shift will be obtained by placing prisms 1 and 2 at the eye-end of the tube, and prisms 3, 4 at the end next the object. Rays will thus have to travel over the length of the tube three times in succession.

By this combination of reflecting prisms with the lenses of the astronomical telescope, we obtain a construction which, as regards handiness, field of view, and illumination, leaves nothing to be desired. The two arrangements of prisms above described were

invented many years ago by Porro, an Italian engineer, but attracted little attention.<sup>1</sup>

**Lateral Shifting** can be increased by separating No. 1 prism in the first arrangement, or No. 4 in the second, from the three remaining prisms. This shortens the telescope, but adds to its width. The separated single prism can conveniently be mounted in the holder of the objective, and the remaining group of three in the holder of the ocular.

Two other advantages (not contemplated by Porro) are also obtained.

In the first place, by reason of the crookedness of the course of the rays, the observer can see without exposing himself.

In the second place—what is of more practical importance—a binocular can be employed in which the two objectives are at a much greater lateral distance than the two eyes, thus giving increased stereoscopic effect; a result which Helmholtz endeavoured to obtain in his telestereoscope<sup>2</sup> by employing two terrestrial telescopes with a principal plane mirror and a reflecting prism.

**56. Zeiss' Field-Glasses and Relief Binoculars.** Porro's two constructions were so completely forgotten that they were several times reinvented, especially the form represented in fig. 13. It was through the Jena Optical Factory that prism telescopes first came into general use.<sup>3</sup> The long delay in utilising so old an

<sup>1</sup> The first is described in the French magazine *Cosmos*, edited by Moigno, vol. 2, p. 222 (1853); the second, with spherical prism-faces, in the same journal, vol. 9, p. 401 (1856).

<sup>2</sup> *Handb. d. Phys. Opt.*, 1st ed. p. 681; 2nd ed. p. 831.

<sup>3</sup> Some historical information respecting prism telescopes will be found in Czapski's book, *On New Kinds of Telescopes, especially for Hand Use*, Berlin, 1895.

R. Steinheil (*Vereinsblatt d. deutsch. Ges. f. Mech. u. Opt.* (1896), p. 2) gives the following testimony:

"Among a number of old models left by my grandfather, C. A. Steinheil, I found a few days ago a small metal case of peculiar shape, with two round openings on opposite sides of the case but not directly opposite, which, on closer examination, turned out to be an inverting assemblage of prisms. [It was a compact form of the second arrangement.] One of the two openings in the case had a screw thread, obviously for receiving the objective, and the other was obviously intended for receiving the sliding ocular tube." The date is believed to be "about 1830, as at that time C. A. Steinheil was much occupied with apparatus in which prisms played a leading part."

idea may partly be explained by the difficulty arising from the length of path in glass and consequent large absorption in traversing the system of prisms; this length being much greater in the prism telescope than even in the ordinary terrestrial telescope. The Jena Glass Works furnished for the first time the means of overcoming this difficulty. Indeed, of all the glasses in the Jena list, there are only two which are sufficiently transparent for telescope prisms, and only one of the two is really available, as the other cannot be obtained free from bubbles.

The starting point of this new line of work may be found in the fact that some of the scientific advisers of the firm—quite unaware of what Porro had done—were impressed with the advantage that might be derived from the lateral shift obtainable by successive reflections.

Two types of prism telescope are made by the firm of Zeiss.<sup>1</sup> For field-glasses, they employ the arrangement described (in the first half of article 55) as giving maximum shortening. For relief binoculars, which are the practical realisation of Helmholtz' conception of a stereoscopic telescope, they employ one of the methods of giving large lateral shift described in the beginning of the second half of the article.

The widening-ratio, that is, the ratio of distance between objectives to distance between oculars (both measured from centre to centre) ranges from 1.75 to 2 in field-glasses, and from 5 to 7 in relief binoculars. A relief telescope with stand was exhibited at the Munich International Congress of Psychologists in 1896, in which the distance between the objectives was 15.2 cm., so that, taking the distance between the eyes as 6.2 cm., the widening-ratio was between 24 and 25. According to the report by G. Hirth, the performance of the instrument corresponded to these figures.

**57. Increase of Resolving Power and Illumination in Telescopic Objectives.** The resolving power of a telescope is determined by the linear aperture of its objective. Let  $\delta$  denote the angle between two fine lines or points, for example, two stars, which are just separable,  $b$  the linear aperture (*i.e.* the clear

<sup>1</sup> Prospectus of Binoculars, 1897.



diameter of the objective), and  $\lambda$  the mean wave-length of the light, then we have<sup>1</sup>

$$\delta = \frac{\lambda}{b}.$$

The brightness of the image of a body subtending a sensible angle is proportional to  $Qb^2$ , if we denote by  $Q$  the ratio of the transmitted to the incident light. We shall use a symbol  $H$  defined by

$$H = Qb^2 \dots\dots\dots(1)$$

It is desirable, even for small objectives, that  $Q$  should be as near to unity as possible; but this element comes much more into consideration in the case of large objectives; as will appear, if we examine the connection between increase of diameter of the objective and increase of brightness of the image.

Equation (1) gives

$$\frac{1}{H} \frac{dH}{db} = \frac{2}{b} + \frac{1}{Q} \frac{dQ}{db} \dots\dots\dots(2)$$

$Q$  depends partly on loss by reflection and partly on loss by absorption.

The ratio of the light transmitted through one of the surfaces to the light incident on the surface, is, for normal incidence, according to Fresnel,

$$R = 1 - \left( \frac{n-1}{n+1} \right)^2, \dots\dots\dots(3)$$

$n$  denoting the mean index of refraction.

Again, if  $K_a$  denote the ratio of the transmitted to the entering light for thickness  $\alpha$ , and  $K_\beta$  the corresponding ratio for thickness  $\beta$ , we have

$$K_\beta = (K_a)^{\beta/\alpha} \dots\dots\dots(4)$$

Now consider an objective composed of two lenses whose indices inserted in (3) give values  $R_1$  and  $R_2$ ; supposing  $K_a$  to be known by experiment for a certain thickness  $\alpha$ , and to have the same value for both lenses; the total thickness being  $\beta$ .

In computing the resultant effect, each of the factors  $R_1$ ,  $R_2$

[<sup>1</sup> See Everett's *Illustrations of C.G.S. Units*, 1902 edition, Art. 148.]

will occur twice, because each lens has two surfaces. The ratio of the transmitted to the incident light for the complete objective will therefore be

$$Q = R_1^2 R_2^2 K_\beta = R_1^2 R_2^2 K_a^{\beta/a} \dots\dots\dots(5)$$

The thickness  $\beta$  may be taken at from  $1/6$  to  $1/7$  of the diameter  $b$ . Taking then  $\beta = b/6.5$ , we find

$$\frac{1}{H} \frac{dH}{db} = \frac{2}{b} + \frac{1}{6.5a} \log_e K_a \dots\dots\dots(6)$$

The first term  $2/b$  is positive, and diminishes as  $b$  increases. The second term is independent of  $b$ , and is negative, since the fraction  $K_a$  is less than unity. For small values of  $b$ , the positive term is large compared with the negative, and absorption does not much influence the change of brightness with change of size; but the case is different when  $b$  is large. It is theoretically possible for  $b$  to be so large that the positive and negative terms cancel each other, indicating that the brightness has reached a maximum and further increase of size will involve loss of light. This limit is never reached in practice, but there is a limit beyond which the advantage gained by enlargement would be too small to justify the additional outlay; and this limit depends, as equation (6) shows, on the value of  $K_a$ , the limit being carried further as  $K_a$  approaches unity.

**Practical Example.** Transparency is specially important in telescopes intended for photography. Hence the data found by H. C. Vogel<sup>1</sup> for the objective designed for the great refractor recently erected at Potsdam will serve as a very appropriate illustration. Having regard to the purpose for which it was intended, and to the results of preliminary experiments, it was decided to achromatise the objective for chemical rays only, and to attach to the instrument a guiding telescope of the same focal length.<sup>2</sup> Steinheil, the maker, proposed as suitable glasses, the light flint O. 340 and the crown O. 203, which could be had in large pieces without faults; hence an examination of the absorbing properties of these two glasses was undertaken.<sup>3</sup> The results, so far as they concern us, are here summarised.

<sup>1</sup> *Math. u. naturw. Mitteil. der Berlin. Akad.*, 1896, vol. 9, p. 623.

<sup>2</sup> See Art. 60.

<sup>3</sup> See Art. 25.

Values of  $K_a$  for  $a = 10$  cm.

	O. 340	O. 203.
Visual rays, - - -	0.84	0.85
Photographic rays, -	0.615	0.692

Substituting accordingly for  $a$  and  $K_a$  in equation (6), we obtain

$$\text{for visual rays } \frac{1}{H} \frac{dH}{db} = \frac{2}{b} - .0027, \dots\dots\dots(7a)$$

$$\text{for photographic rays } \frac{1}{H} \frac{dH}{db} = \frac{2}{b} - .0066, \dots\dots\dots(7b)$$

the unit of length being the centimetre.

The right-hand member of (7a) vanishes for about  $b = 750$ , and that of (7b) for about  $b = 300$ . The maximum of visual brightness would accordingly be reached with an objective of  $7\frac{1}{2}$  metres diameter, and that of photographic intensity with one of 3 metres. The diameter actually decided on was 80 cm., which is greater than that of any other objective in Europe.<sup>1</sup>

For the guiding telescope an aperture of about 50 cm. was adopted, the focal length being in both cases 12 m. The ratios of aperture to focal length were accordingly 1/15 and 1/25.

Putting  $b = 80$  in equation 7b, we get

$$\frac{1}{H} \frac{dH}{db} = .0184.$$

This is the ratio of  $dH$  to  $H$  for an increase of 1 cm. in  $b$ . Increasing the aperture from 80 cm. to 81 cm. would accordingly increase the photographic intensity 1.84 per cent. The increase in area would be 2.5 per cent. Increasing the diameter to 100 cm. would increase the intensity by less than 40 per cent., and would not repay the additional outlay.

**Table for calculating Intensity of Illumination for Objectives of Different Sizes.** As glasses O. 340 and O. 203, or others with nearly the same properties, are likely to be frequently employed for a similar purpose, Vogel has calculated the following table applicable to them :

[<sup>1</sup> The objective made about the same time for the Meudon observatory is a trifle larger.]

$\beta$ cm.	100 $K_\beta$		100 $Q$	
	Visual.	Photographic.	Visual.	Photographic.
4	93	84	77	69
6	90	77	75	63
8	87	71	72	58
10	84	65	70	53
12	82	60	67	49
14	79	55	65	45
16	76	50	63	41
18	74	46	61	38
20	71	43	59	35
22	69	39	57	32
24	67	36	55	29
26	65	33	53	27
28	62	30	52	25
30	60	28	50	23
32	58	25	48	21
34	56	23	47	19
36	55	21	45	18
38	53	20	44	16
40	51	18	42	15

In computing the table,  $K_a$  for  $\alpha = 10$  cm. was taken as .845 for visual, and .653 for photographic rays. The value of  $Q$  depends partly on  $R_1$  and  $R_2$ , which were computed by equation (3); the values assigned to  $n$  in computing  $R_1$  being 1.583 for visual and 1.601 for photographic, and in computing  $R_2$ , 1.521 and 1.532, these being the indices for the line  $b_1$  (wave-length  $.518\mu$ ) and the line  $h$  (wave-length  $.410\mu$ ).

In using the table to find the value of  $H$  or  $Qb^2$ ,  $\beta$  may be taken as from  $\frac{1}{8}$  to  $\frac{1}{4}$  of  $b$ .

The two glasses above discussed are Nos. 13 and 64 of the list in Art. 17, and are described as "ordinary silicate crown" and "ordinary light flint." The baryta light flints are even more free from colour. The improved method of annealing large discs introduced at the Jena Works is another important contribution to astronomical requirements.

**58. Cemented Doublets for Objectives.** In an objective consisting of two lenses not in contact, there are four radii of



curvature disposable. By means of these, it is possible to give a prescribed focal length, to achromatise, to correct for spherical aberration on the axis, and to satisfy the sine-condition. The marginal aberration will, as a consequence, be practically annulled, if the ratio of focal length to aperture is not too small.<sup>1</sup> These are the general requirements for all good telescopic objectives. Expressions for the four radii, deduced from the four above-mentioned conditions, are given at the end of a paper by Moser on astronomical objectives.<sup>2</sup>

If, for small objectives, say, of less than 50 mm. aperture, the further condition be imposed that the two lenses shall be in contact over one surface of each, there will be only three radii disposable; and the question arises what glasses must be used in order that the requirements may still be satisfied.

H. Harting's investigation of this question by calculation<sup>3</sup> leads to the conclusion that, with the glasses available down to 1884, it is impossible to produce cemented doublets which, in addition to being achromatic and free from axial aberration, will also rigorously satisfy the sine condition. In all pairs of crown and flint, the dispersion of the crown is too high, and that of the flint too low, in comparison with the index. Hence in pencils oblique to the axis more or less aberration remains.

It is true that, in some of the old pairs of glasses, this outstanding aberration did not practically matter, for the simple reason that they had other worse faults, compared to which it was unimportant. This is the case, for example, in the following objective (crown in front) which belongs to a type formerly common:

	$n_D$
Crown O. 40,	1.5166
Flint O. 167,	1.6169

$$r_1 = +0.4117; \quad r_2 = -0.4155; \quad r_3 = +47.62;$$

$$\frac{1}{r_1} - \frac{1}{r_3} = 2.41.$$

The values of the three radii of curvature are expressed in terms

<sup>1</sup> See Czapski, Winkelmann's *Handb. d. Phys.*, II. 1, 270.

<sup>2</sup> *Zeitschr. f. Instrum.*, 7, 225 (1887).

<sup>3</sup> *Zeitschr. f. Instrum.*, 18, 357 (1898).

of the focal length taken as unity. The difference given in the last line is the external curvature.

On the other hand, the new Jena glasses permit a strict or nearly strict fulfilment of the sine condition, and that in two ways :

First, by combining a silicate flint of index 1.64 to 1.65, with a borosilicate crown of index 1.50 to 1.51, and of smaller dispersion than the old crowns ; for example,

	$n_D$
Flint (in front)	O. 102, 1.6485
Borosilicate crown	O. 144, 1.5100

$$r_1 = +0.4234; \quad r_2 = +0.2446; \quad r_3 = -14.71;$$

$$\frac{1}{r_1} - \frac{1}{r_3} = 2.43.$$

Here the sine condition is strictly fulfilled. The external curvature, however, is somewhat greater than in the preceding objective, and this is disadvantageous for avoiding axial spherical aberration.

Secondly, by combining a barium-silicate crown of index 1.57 to 1.59, with a flint whose index need only be slightly greater ; for example,

	$n_D$
Baryta crown (in front),	1.5899
Baryta flint,	1.6229

$$r_1 = 0.6473; \quad r_2 = -0.3059; \quad r_3 = -3.175;$$

$$\frac{1}{r_1} - \frac{1}{r_3} = 1.86.$$

In this objective, the sine condition is very nearly fulfilled, and the external curvature is considerably lessened. Hence, with this objective, the aperture may be made decidedly larger,<sup>1</sup> compared with the focal length, than would be permissible with crown and flint having large difference of index.

The solution of this special problem in the optics of the telescope is thus considerably furthered by the new Jena glasses.

**59. Astigmatism and Curvature of Image in Astronomical Objectives.** The question whether the astigmatic curvature of the image formed by an astronomical objective can be materially

<sup>1</sup> See Czapski, *loc. cit.*, 271.

diminished by proper choice of glasses, has been examined by H. Harting by means of approximate algebraic formulae.<sup>1</sup> These formulae are based on the three assumptions:

That the thicknesses of the lenses composing the objective are negligible;

That the axes of oblique pencils from infinitely distant points pass through the centre of the objective;

That the inclinations of these axes to the optic axis do not exceed about  $5^\circ$ .

From these assumptions it is immediately deduced, that the astigmatic difference (distance between primary and secondary focus, divided by focal length)<sup>2</sup> is equal to the square of the inclination. Thus, for an inclination of  $5^\circ$ , the distance is about  $\frac{3}{4}$  per cent. of the focal length.

Since this amount on the assumed hypothesis is invariable, it remains to be seen whether it is possible to make the two astigmatic image-surfaces symmetrical with respect to the plane through the focus at right angles to the optic axis. If this be also impossible, the only way left of effecting an improvement is to bring the two image-surfaces nearer to the focal plane.

Beginning with an objective consisting of two lenses, it is found that, other things being equal, it makes no difference in the two astigmatic image-surfaces whether crown or flint be in front. It also makes no difference in this respect whether only two lenses are used or a larger number, so long as only two kinds of glass are employed. It is only by introducing more than two kinds of glass that the curvature is changed.

After this preliminary discussion, Harting confines himself to objectives made of only two kinds of glass. Let  $n, \nu$  refer to the crown, and  $n', \nu'$  to the flint, with the assumption  $\nu > \nu'$ . Then, if  $\rho_s$  and  $\rho_t$  be the curvatures of the secondary and primary image-surfaces (the focal length of the objective being taken as the unit of length), we have

$$\left. \begin{aligned} \rho_s &= 1 + \sigma \\ \rho_t &= 3 + \sigma \end{aligned} \right\}, \dots\dots\dots (1)$$

$$\text{where} \quad \sigma = \frac{\nu}{\nu - \nu'} \left( \frac{1}{n} - \frac{1}{n'} \right) + \frac{1}{n'} \dots\dots\dots (2).$$

<sup>1</sup> *Zeitschr. f. Instrumentenk.*, 19, 138, (1899).

<sup>2</sup> See Art. 46.

Both  $\rho_s$  and  $\rho_t$  are regarded as positive when the corresponding surfaces are concave towards the objective.

In all the glasses under consideration,  $\sigma$  is positive. Hence it is not possible to attain symmetry as regards the two image-surfaces; for this would require  $\rho_s + \rho_t = 0$ , whence  $\sigma = -2$ .

Further, any considerable flattening of the image-surfaces by diminution of  $\sigma$  could only be attained by an "anomalous" pair (see Art. 47) in which  $n > n'$  and  $\nu > \nu'$ . The first term in the expression for  $\sigma$  then becomes negative, and can be increased numerically by diminishing the difference  $\nu - \nu'$ . A limit is, however, set to this diminution by the requirements of spherical and chromatic correction.

Thus no marked diminution of astigmatism or of curvature of image can be effected by selection of glasses.

**60. Chromatic Aberration in Objectives of Great Focal Length.** The length of the secondary spectrum may become very considerable with increased focal length. We have a good example of this in the great instrument of the Lick Observatory. The following table gives the relative positions of its chromatic foci, from Keeler's measurements:

Ray.	Wave Length.	Position of Focus.
<i>B</i>	·6867 $\mu$	0·0 mm.
<i>C</i>	·6563	- 6·1
<i>D</i>	·5893	- 11·4
<i>F</i>	·4862	0·0
<i>G'</i>	·4341	+ 36·8
<i>h</i>	·4102	+ 70·1

The objective, as the table shows, is achromatised for the visual rays by uniting *B* with *F*. The positions of the other foci are specified with reference to this point of union, the plus sign indicating greater distance from the objective. The focal length of the objective is about 17·4 m.

The shortest chromatic focal length belongs to a green ray, and corresponds to -11·9 in the notation of the table. The length of the spectrum within the limits of the table is therefore 82 mm. The focal curve plotted (as in Art. 19), from the data



given in the table has the form characteristic of the old optical glasses.

The visual focus of the objective lies at the point of union of the complementary red and green, at  $-5.1$ . The greater portion of the remaining rays are not helpful for the visual image, but tend to blur it.

The photographic rays have an ill-defined focus at about  $+41.9$  from the assumed zero point. Thus the distance between the visual and photographic foci is about 47 mm. The imperfect achromatism of the objective for chemically active rays becomes unpleasantly evident when the telescope is used for photography, or for spectrographic observation of the more refrangible rays. A correcting lens placed before the objective brings about a better union of the actinic rays, and at the same time shortens the focal length considerably.<sup>1</sup>

The secondary spectra of the Potsdam 29.8 cm. refractor, and the Vienna 67.5 cm. refractor, have been investigated by H. C. Vogel, from whose papers the following data are taken:<sup>2</sup>

Potsdam Refractor.		Vienna Refractor.	
Wave Length.	Position of Focus.	Wave Length.	Position of Focus.
.690 $\mu$	+ 4.2 mm.	.690 $\mu$	+ 2.1 mm.
.610	+ 0.3	.610	- 6.7
.530	- 1.7	.570	- 7.8
.486	0.0	.486	0.0
.470	+ 1.6	.470	+ 4.4
.430	+ 9.2	.430	+ 20.7
.410	+ 16.7	.410	+ 31.1

The Potsdam instrument is achromatised by uniting  $F$  with a line near  $D$ ; the Vienna one by uniting  $F$  with a line near  $C$ .

In view of the above results it was decided that the objective of the great refractor, of 80 cm. aperture and 12 m. focus (see Art. 57), to be erected at Potsdam for photographic purposes,

<sup>1</sup> The reference for these particulars is D. Taylor, *Improvements in Compound Object-glasses for Telescopes* (1893).

<sup>2</sup> *Monatsber. d. Berlin. Akad.*, 1880, 438, and *Publ. d. astrophys. Obs. zu Potsdam*, IV. 1, 4. Also *Ber. d. Berl. Ak.*, 1896, 1221; and *Mathem. u. Naturw. Mitt.*, 1896, 625.

should be achromatised for the most powerfully actinic rays. It was at first intended to equip the large telescope with an appliance for introducing or removing at will a system of lenses for bringing about a better union of the visual and chemical rays. This, however, would have required a triple lens, which, in order to give a fairly large field, must have had a diameter not less than 30-40 cm. On account of the expense involved, and for other reasons, the plan was given up, and the only means of correction provided was Christie's arrangement of a small doublet near the focus—largeness of field being sacrificed. This correcting lens is used when spectrum observations are to be made in the less refrangible part of the spectrum.

The auxiliary eye telescope of 50 cm. aperture and 12 m. focus is itself a powerful instrument—more powerful than any telescope previously constructed in Germany.

The foregoing data clearly show that the removal of the secondary spectrum is a pressing problem in telescopic optics.

If the chromatic remnant of spherical aberration could be removed, this also would have a beneficial effect on the image. We shall deal in the next article with the attempts hitherto made to solve these two problems.

**61. Removal of Secondary Spectrum in a Double Objective by Phosphate Crown and Borate Flint.** The two glasses S.30 and S.8 (Nos. 3 and 24 in the list of Art. 17) are specially suitable for mutual achromatisation in a double objective. If the foci for the *C* and *F* rays are united on the axis, and the focus for *D* be taken as origin, the residual aberrations are found, by calculation, to have the following values in mm. per metre of focal length:

<i>A'</i>	<i>C</i>	<i>D</i>	<i>F</i>	<i>G'</i>
-0.07	+0.07	0.00	+0.07	+0.49

The dispersion is thus almost entirely abolished from *A'* to *F*, becoming appreciable only beyond *F*, and quite small even there. The character of a tertiary spectrum, such as this, is easily gathered from a glance at the focal curve (2) of Art. 19.

Czapski has calculated the outstanding chromatic aberrations for the same pair of glasses when so combined that the focal length is a minimum for  $\lambda_0 = .55\mu$  (which is about the brightest

place in the solar spectrum), according to the method described in Art. 20. The following are the results, expressed in the same units as before:<sup>1</sup>

$\lambda =$	$0.77\mu$	0.73	0.69	0.65	0.61	0.57	0.55	0.53	0.49	0.45	$0.41\mu$
	-0.04	-0.02	-0.01	0.00	0.00	0.00	0.00	+0.01	+0.04	+0.21	+0.79

The aberrations from  $\lambda = .77\mu$  to  $\lambda = .49\mu$ , that is, from  $A'$  to  $F'$ , are here even more completely corrected, the general character of the focal curve remaining unchanged.

**Testing of Objectives of S. 30 and S. 8.** Two objectives, each composed of the two glasses in question (a phosphate crown and a borate flint) made by Bamberg of Berlin from Czapski's calculations, were tested by H. C. Vogel for their actual achromatism by a method of his own, distinguished by the sharpness of its indications.<sup>2</sup>

If the image of a bright star, formed by a powerful astronomical telescope, is viewed through a direct-vision train of prisms, the image of the star is drawn out into a spectrum; and this spectrum cannot, by any adjustment of focus, be reduced to a sharp line. It may rather be described as a diffuse band constricted in one or two places and widening out at the violet end. This is due to incomplete achromatism of the objective.

Suppose, for example, that the objective is composed of the crown O. 60 and the flint O. 103, which, when combined, give the focal curve (1) of Art. 19. When the eyepiece is focussed for the part of the spectrum where the focal length is least, which, as the figure of Art. 19 shows, is a little above  $D$ , the spectrum



FIG. 14.

will be narrowed down near  $D$ , and will broaden out towards both ends, because the spectrum is increasingly out of focus. It will therefore have the form roughly sketched in fig. 14,  $a$ .

<sup>1</sup> Winkelman, *Handb. d. Physik*, II. 1, 146.

<sup>2</sup> *Monatsber. d. Berlin. Akad.*, 1880, 433.

As the eyepiece is pulled further out, the constriction will break up into two, which will travel in opposite directions; and when one has reached  $F$ , the other will be at  $C$ , as shown in fig. 14, *b*. In like manner all the lines seen in the spectrum of the star can be brought one at a time into focus; and the positions of the eyepiece will show the relative positions of the different chromatic foci. By plotting these observations, with the wave-lengths as abscissae, empirical focal curves are obtained which can be compared with the theoretical curves, and will show to what extent theoretical expectations have been fulfilled.

Vogel began by applying this method to four objectives by Schröder, Grubb, Fraunhofer, and Steinheil, using the star Sirius; and secondary spectra of large range were exhibited. The pairs of coincident foci are different for the different objectives; but the distribution of the foci for the most important visual rays—say from  $C$  to  $F$ —is nevertheless practically the same for all. If the distance from the focus of  $F$  to that of  $G'$  is also taken into consideration, the Fraunhofer objective is distinctly superior to the others. Since it, therefore, is the most suitable for comparison with more completely achromatised objectives, we subjoin a list of its chromatic aberrations.

#### FRAUNHOFER TELESCOPE AT BERLIN OBSERVATORY.

Aperture 24.3 cm.; Focal Length 433.1 cm.

Ray.	$\lambda$ .	Pulling Out.	Per Metre Focal Length.
	0.690 $\mu$	- 0.8 mm.	- 0.19 mm.
<i>C</i>	.656	- 1.3	- 0.30
<i>D</i>	.590	- 2.8	- 0.65
<i>b</i>	.517	- 1.2	- 0.28
<i>F</i>	.486	0	0
	.459	+ 1.8	+ 0.42
<i>G'</i>	.434	+ 4.0	+ 0.92
<i>h</i>	.410	+ 8.5	+ 1.96
<i>H</i>	.397	+ 15.7	+ 3.62

The minimum focal length comes almost exactly at  $D$ . The red ray  $C$  is united to a green ray of about  $\lambda = .525\mu$ , beyond  $E$ . The focus for  $F$  is taken as the zero of the measurements.



The same method was afterwards<sup>1</sup> applied by Vogel to the two objectives mentioned at the beginning of this Article, which were constructed with a view to preliminary trials of the new glasses S. 30 and S. 8. The results are given in the following table, together with the aberrations of the Fraunhofer objective for the same wave-lengths. Of the Fraunhofer values, some are directly observed, and the rest are derived by interpolation from the observed values given in the preceding table.

Objective I. Aperture 13.4 cm.; Focal Length 197.3 cm.  
 Objective II.       "       17.6 cm.;       "       250.0 cm.

$\lambda$	Chromat. Aberr. per metre of Focal Length.		
	I.	II.	Fraunhofer.
0.710 $\mu$	-0.05 mm.	-0.02 mm.	+0.67 mm.
.650	+0.05	+0.05	+0.23
.590	0.00	0.00	0.00
.530	-0.06	-0.10	+0.24
.470	+0.15	+0.05	+0.86
.410	+1.10	+0.40	+2.60

Czapski has pointed out<sup>2</sup> that, in testing extremely well-achromatised small objectives, the results may be seriously affected by the chromatic errors of the ocular and of the eye. He accordingly suggests that the image of the sun formed in a globule of mercury should be viewed through the ocular and prisms, and the errors thus observed subtracted from those observed in the principal test. Vogel took this suggestion into account in his deduction of the above results.<sup>3</sup>

In discussing the above comparisons Vogel remarks on the extraordinary advance in achromatisation which they exhibit, and its importance for spectrographic work, in view of the fact that with the great telescopes of the present day, it is impossible to

<sup>1</sup> *Vierteljahrschr. d. Astron. Ges.*, 22, 142 (1888). Referat: *Zeitschr. f. Instrumentenk.*, 8, 246 (1888).

<sup>2</sup> *Zeitschr. f. Instrum.*, 8, 247 (1888).

<sup>3</sup> Czapski in *Zeitschr. f. Instrum.*, 9, 250 (1889) criticises a method published by Ch. S. Hastings for calculating the secondary spectra of telescopic objectives, and the employment of an objective (of S. 30 and S. 8) of only 6.7 cm. aperture as a test of the method.

obtain a general view of the whole spectrum at once, owing to the wide separation of the foci of the different colours.

On comparing the tertiary spectrum actually obtained with that deduced from theory,<sup>1</sup> satisfactory agreement is found, both as regards the main features of the focal curves, and the order of magnitude of the residual aberration.

**62. Difficulties attending the use of Phosphate and Borate Glasses.** In the attempt to utilise, for the improvement of telescopic objectives, new glasses of favourable optical qualities, such as phosphate and borate glasses, various difficulties are encountered.<sup>2</sup>

For an astronomical objective, discs of large diameter are required, and this may preclude the use of a glass which can be employed without difficulty for other optical purposes.

Again, glasses of essentially new composition have their own peculiar mechanical properties, which, as a rule, render them unfit to be worked by the ordinary methods of an optical factory.

Further, the customary methods of cooling do not suit the new glasses. Stresses which would be of no consequence in ordinary silicate glasses become serious defects in phosphates and borates, and unfortunately the tendency to acquire these stresses during solidification is greater in phosphates and borates than in silicates. It is obvious that this greatly increases the difficulty of making large objectives.

These difficulties, formidable as they appear, have all been overcome. There remains, however, another difficulty, which is inseparably connected with the chemical composition of the glass, namely, its liability to be attacked by moisture. Among the phosphate and borate glasses there are several which cannot safely be exposed to damp air for any length of time.<sup>3</sup>

**63. Successful Employment of Newer Glasses.** Under the circumstances just mentioned, it is not surprising that further attempts are continually being made to discover new glasses which are chemically and mechanically durable, besides possessing the requisite refracting properties.

<sup>1</sup> See early part of this Article.

<sup>2</sup> See Czapski in *The Observatory*, June, 1889.

<sup>3</sup> See Appendix.

That these efforts have been crowned with success appears probable, from an article published by M. Wolf<sup>1</sup> relating to an objective constructed by Zeiss from calculations by M. Pauly, which was tested at the Astrophysical Observatory of Heidelberg. It was composed of two lenses, but particulars of the two glasses employed are not given; the article deals only with results.

The objective had a clear aperture of 21.2 cm., and a focal length of 445 cm.; so that its relative aperture was 1/21. It showed very little absorption for visual rays.

The chromatic aberrations on the axis were determined by Vogel's method, described in Art. 61, the stars employed being  $\alpha$  Herculis,  $\alpha$  Aquilae, and  $\alpha$  Lyrae. The aberrations (per metre of focal length) are given in the column headed "Pauly" in the following table, the focus of  $F$  being taken as the zero-point.

$\lambda$	Chrom. Aberr. per metre Focal Length.	
	Pauly.	Fraunhofer.
0.690 $\mu$	+0.02 mm.	-0.19 mm.
.660	-0.02	-0.30
.590	-0.03	-0.65
.520	0.00	-0.28
.486	0.00	0.00
.434	+0.53	+0.92
.410	+1.16	+1.96

The corresponding aberrations for the Berlin Fraunhofer objective are given for comparison. The chromatic aberrations of the eye were (on principle) not subtracted.

The above values, either taken as they stand, or plotted with wave-length as abscissa, show that the secondary spectrum, from the red to a little beyond  $F$ , is practically abolished. As Wolf remarks, the new objective is so much better than the old ones, that "comparison is out of the question. It practically focuses all the visual rays in one plane." Any remnant of chromatic aberration for visual rays "can only be measured by careful examination with high powers."

<sup>1</sup> *Zeitschr. f. Instrum.*, 19, 1 (1899).

And the advantage is not confined to spectrographic work. "Surprisingly beautiful were the perfectly colourless images of moon-craters and sun-spots; which possessed a quite unique charm, and, under a power of 825, showed unusual details."

"On four evenings, in spite of rather stormy weather and unsteady air, the separating power of the new objective for close double-stars was tried. The following pairs were well separated:<sup>1</sup>

$\eta$ Coronae,	distance	0".4	magnitudes	5	and	6
$\mu_2$ Bootis,	"	0".9	"	7	"	8
1 Coronae,	"	0".8	"	6	"	7
$\gamma$ Coronae,	"	0".4	"	4	"	7
$\lambda$ Cassiopeiae,	"	0".6	"	6	"	6
$\mu$ Cygni,	"	2".9	"	4	"	5
$\zeta$ Herculis,	"	0".5	"	3	"	7
O $\Sigma$ 338,	"	0".7	"	6 $\frac{1}{2}$	"	6 $\frac{1}{2}$
$\Sigma$ 2695,	"	0".9	"	6	"	8

the only one that gave any trouble being  $\zeta$  Herculis. The pairs  $\zeta$  Bootis and 52 Arietis could not be separated.

"The diffraction rings were beautifully shown. The discs were absolute circles, and I found, with Dr. Schwassman's assistance, from numerous estimates aided by known distances of double stars," the following diameters of star discs:

Stars of 6 <sup>th</sup> magnitude.	Diameter	0".24.
" 6 $\frac{1}{2}$	"	0".24.
" 8	"	0".15.

These tests establish "the great superiority of the new objective, which combines the steadiness of the refractor with the colourlessness of the reflector."

The surface of the glass showed itself to be "fully resisting and durable."

#### 64. Suppression of Residual Spectrum in Triple Objective.

In the triple objective constructed from H. D. Taylor's calculations by Cooke of York, achromatism is effected in the following way.<sup>2</sup>

[<sup>1</sup> Dawes' rule for the limit of separability gives 0".55 as the limit for an aperture of 21.2 cm.]

<sup>2</sup> Improvements in compound object-glasses for telescopes, English Patent, No. 17994 (1893).



Let the thicknesses and distances of the three single lenses be small enough to permit the use of the equation

$$\phi = k(n-1) + k'(n'-1) + k''(n''-1), \dots\dots\dots(1)$$

which is an extension of equation (1) of Art. 18 from two lenses to three,  $k, k', k''$  denoting the total curvatures of the three lenses,  $n, n', n''$  their indices for any one value of  $\lambda$ , and  $\phi$  the reciprocal of the focal length of the system for this wave-length.

When  $\lambda$  changes from one given value to another, let the corresponding changes of  $n, n', n''$  be  $\delta, \delta', \delta''$ ; then we have

$$\text{Change of } \phi = k\delta + k'\delta' + k''\delta''. \dots\dots\dots(2)$$

Now introduce the condition  $k'' = k'$ ; then we have

$$\phi = k(n-1) + k'(n'-1 + n''-1), \dots\dots\dots(1a)$$

$$\text{Change of } \phi = k\delta + k'(\delta' + \delta''). \dots\dots\dots(2a)$$

(1a) applied to the  $D$  line gives

$$\frac{1}{d} = k\nu\Delta + k'(\nu'\Delta' + \nu''\Delta''); \dots\dots\dots(1b)$$

and if  $\phi$  is to be the same for  $C$  as for  $F$ , (2a) gives

$$0 = k\Delta + k'(\Delta' + \Delta''), \dots\dots\dots(2b)$$

the notation being that of Art. 18.

From (1b) and (2b) we obtain

$$k = -\frac{1}{d} \frac{\Delta' + \Delta''}{\Delta} \frac{1}{(\nu' - \nu)\Delta' + (\nu'' - \nu)\Delta''},$$

$$k' = \frac{1}{d} \frac{1}{(\nu' - \nu)\Delta' + (\nu'' - \nu)\Delta''}.$$

Substituting these values in the general equation (2a), we find, for change from one arbitrary value of  $\lambda$  to another,

$$d \times \text{change of } \phi = \frac{\Delta' + \Delta''}{(\nu' - \nu)\Delta' + (\nu'' - \nu)\Delta''} \left\{ \frac{\delta' + \delta''}{\Delta' + \Delta''} - \frac{\delta}{\Delta} \right\}; \dots\dots(3)$$

which shows that  $\phi$  is independent of  $\lambda$  if, for all changes of  $\lambda$ ,  $\frac{\delta' + \delta''}{\delta}$  has the constant value  $\frac{\Delta' + \Delta''}{\Delta}$ ; in other words, if  $\frac{\delta' + \delta''}{\delta}$  has any constant value for all parts of the spectrum (since  $\Delta, \Delta', \Delta''$  are particular values of  $\delta, \delta', \delta''$ ).

Calling the three lenses  $L, L', L''$ , the expressions for  $k$  and  $k'$  show that, if  $\nu$  is the least of the three  $\nu, \nu', \nu''$ ,  $k$  is negative and  $k'$  positive; that is,  $L$  is concave and  $L'$  and  $L''$  are convex, the total curvatures of the two latter being equal.

**Choice of Glasses.** The three following glasses were chosen by Taylor as suited to his purpose:

For  $L$ , Borosilicate flint O. 658;  $\Delta = .01089$ ;  $\nu = 50.2$ .

„  $L'$ , Baryta light flint O. 543;  $\Delta' = .01115$ ;  $\nu' = 50.6$ .

„  $L''$ , Silicate crown O. 374;  $\Delta'' = .00844$ ;  $\nu'' = 60.5$ .

O. 658 is a glass replacing O. 164, No. 25 in the list of Art. 17  
O. 543 is No. 58, and O. 374 is No. 47.

How far the combination of these three glasses satisfies the theoretical condition of complete achromatism found above may be judged from a comparison of the last two columns of the following table:

Interval.	$\delta'$ O. 543	$\delta''$ O. 374	$\frac{\delta' + \delta''}{\Delta' + \Delta''}$	$\frac{\delta}{\Delta}$
$CF$	.01115	.00844	1	1
$A'C$	.00374	.00296	.3420	.3425
$DF$	.00790	.00593	.7059	.7052
$EF$	.00369	.00274	.3282	.3278
$FG'$	.00650	.00479	.5763	.5767
$FH_1$	.01320	.00976	1.1730	1.1745

The dispersions  $EF$  and  $FH_1$  have been calculated from Cauchy's dispersion formula, and are subject to some uncertainty.

The positions of the chromatic foci as calculated from the data are:

	mm. per metre focal length.
$A'$	— .107
$C$	000
$D$	+ .150
$E$	+ .086
$F$	.000
$G'$	+ .086
$H_1$	+ .322

The resulting curve of focal lengths has, like the curve (2) of Art. 19, the double bend characteristic of a tertiary spectrum; but the bends are moved higher up the spectrum, so that the triple union, instead of extending from  $A$  to  $F$ , extends from  $C$  to a little beyond  $G'$ .

**An Objective of 15.2 cm. Aperture and 274 cm. Focal Length** is described by Taylor in detail. It is composed as follows :

$L'$	$L$	$L''$
$r_1' = +102.7$ cm.	$r_1 = -34.8$ cm.	$r_1'' = 23.9$ cm.
$r_2' = -34.8$ "	$r_2 = +23.9$ "	$r_2'' = 44.7$ "
Thickness 1.5 "	Thickness 0.3 "	Thickness 1.5 "
Distances, -	$LL = 0.0$ mm.	$LL'' = 0.2$ mm.

Thus the negative lens is between the two positive ones, the baryta flint being in front. The thicknesses given are for the centres. There are only 4 different radii of curvature.

Among the special advantages of this construction, Taylor mentions particularly the getting rid of the chromatic remnant of spherical aberration.

The aperture ratio is  $1/18$ . In smaller objectives it may be  $1/15$ .

Taylor also expounded the advantages of his objective at a meeting of the Royal Astronomical Society,<sup>1</sup> and was able to announce that its actual performance corresponded to theoretical expectation. The misgivings expressed at the meeting by Grubb and Ranyard, as to the durability of the borosilicate glass employed, were probably due to their confounding it with borate flint, which is not fitted to bear exposure.

**65. Two-part Gaussian Objective.** The actual range of distribution of the chromatic foci along the axis of an objective is not the same thing as the length of the secondary spectrum of that particular zone of the objective which has been achromatised; for if spherical aberration is, as usual, corrected for only one colour, the chromatic difference of spherical aberration will materially increase the length. In the objective which bears Gauss' name, spherical aberration is theoretically annulled for two colours. By this means the displacement of the chromatic

<sup>1</sup> *The Observatory*, 17, 132 (1894).

foci in passing from the centre to the edge of the objective can be practically abolished. Gauss' condition for obtaining this result can be fulfilled, besides the three conditions of given focal length, achromatism, and spherical correction on the axis, when four refracting surfaces are disposable. The objective can accordingly be made of two uncemented or three cemented lenses.

Objectives of the Gaussian construction have been calculated both by S. Czapski and by O. Lummer, consisting, in each case, of a positive lens of phosphate crown and a negative of silicate flint. The flint is placed in front, as the opposite arrangement would require excessively large external curvatures.

**Czapski's Objective.** Two objectives, made by Bamberg of Berlin from Czapski's calculations, were exhibited on the occasion of the Naturforscher meeting in Berlin (1886), and have been described by Krüss<sup>1</sup> from data furnished by Czapski. In his paper, from which all the details below are taken, the following indices are given for the crown lens  $L$  and the flint  $L'$ .

	$A$	$C$	$D$	$F$	$G$
$n$	1.57036	1.57342	1.57605	1.58226	1.58725
$n'$	1.60682	1.61153	1.61558	1.62540	1.63350

The values for the crown glass agree with those given for the heavy barium phosphate No. 3 of Art. 17.

The dimensions of the objective are :

Flint	$r_1 = -$	226.0 mm.	Thickness, flint	7.5 mm.
	$r_2 = -$	400 "	" crown	12.0 "
Crown	$r_3 = -$	1256.0 "	Interval,	2.0 "
	$r_4 = -$	278.7 "	Aperture,	134 "

In the achromatising,  $C$  and  $F$  were united. The spherical aberration was corrected for  $D$ .

The headings  $c, d, f$  in the following table denote the distances of the chromatic foci for  $C, D, F$  from the last face of the objective. They are given for three different narrow zones,

<sup>1</sup> See page 60 of "A comparative investigation of a number of objectives in which Gauss' condition is fulfilled"; *Zeitschr. f. Instrum.*, 8. 7, 53, 83 (1888).



namely, the central zone, the marginal zone, and a zone  $\frac{2}{3}$  of the way from centre to margin.

	<i>c</i>	<i>d</i>	<i>f</i>
Central zone	2085.99 mm.	2085.51 mm.	2085.94 mm.
Intermediate zone	2085.96 „	2085.38 „	2085.82 „
Marginal zone	2086.04 „	2085.46 „	2085.72 „

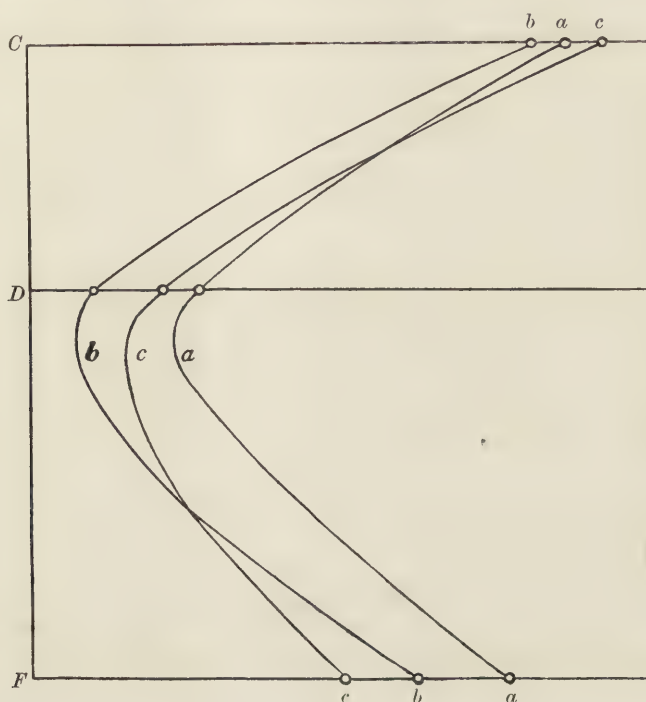


FIG. 15.

Fig. 15 shows the curves of focal length plotted from these values, the curve *a* being for the central zone, *b* for the intermediate, and *c* for the marginal zone. The horizontal distances in the figure are 100 times the actual distances indicated by the table. The curves bring out the following facts.

For all colours between *C* and *D* the central and marginal spectra practically coincide. They begin to separate to a notice-

able extent, a little beyond *D*, and the separation increases as the wave-length diminishes, but only amounts to 0.22 mm. even at *F*.

The union of the spectrum of the intermediate zone with the central between *C* and *D* is not so close. The separation in this case is greatest near *D*, but does not exceed about 0.13 mm. Beyond this, the spectrum of the intermediate zone approaches nearer to the central, and in doing so coincides at one point with the spectrum of the marginal zone.

Assuming that the intermediate zone here chosen is that which diverges most widely from the central, we arrive at the result that the length of the secondary spectrum for the rays between *C* and *F*, which for the central zone would be about 0.50 mm., is increased to about 0.70 (that is, by about 40 per cent.) by chromatic difference of spherical aberration. As the focal length is about 2 m., the length of the spectrum per metre of focal length may be taken as 0.35 mm.

It would be interesting to compare with these results the distances between the chromatic foci of a double objective, not fulfilling the Gauss condition, but having a short tertiary spectrum. Data for an exact comparison are wanting; but some light is thrown on the matter by Wolf's report on the objective discussed in Art. 63.

With the view of testing for spherical aberration, Fraunhofer's old method was employed of blocking out alternately the circumferential and the central part of the objective; focussing on the moon in each case, and measuring the shift of the ocular by means of a microscope. From 24 readings so taken, a difference of .0006 of the focal length was deduced. As we may assume that the focussing in both cases was governed by rays between *C* and *F*, it may be inferred that the length of the spectrum composed of these colours exceeded 0.6 mm. per metre of focal length, or was about double of the length computed for Czapski's objective. But as the determination was by practical trial in the one case, and by theoretical calculation in the other, the comparison is not entitled to much weight.

**Lummer's Objective.** Lummer has remarked<sup>1</sup> that objectives in which chromatic aberration is corrected by Gauss' method are

<sup>1</sup> *Müller-Pouillet, Lehrb. d. Physik.*, 9th ed., II. 1, 230 (1897). The aberrations of the objectives here discussed are calculated by Lummer at p. 573 *et seq.*

suitable for the collimators and observing telescopes of high-class spectrometers;<sup>1</sup> as it is desirable that the image of the slit should be sharp for all colours simultaneously. A spectrometer of precision, constructed by Wanschaff for the Reichsanstalt, has accordingly been fitted with objectives of the Gauss type, calculated by Lummer and made by Bamberg. Their flint lens  $L'$  is of silicate O.102, and their crown lens  $L$  of the glass S.41, which replaces the phosphate crown S.40. They have the following indices:

	$C$	$D$	$F$	$G$
$n$	1.55284	1.55531	1.56113	1.56576
$n'$	1.64373	1.64920	1.66294	1.67475

The dimensions are:

Radii of curvature.

$r_1 = -$	93.27 mm.	Thickness—Flint,	3.6129 mm.
$r_2 = -$	140.24	„ Crown,	5.4193
$r_3 = +$	1212.69	Interval, -	- 0.9032
$r_4 = -$	141.42	Aperture, -	- 50

In the achromatisation  $C$  and  $G$  are united, and spherical aberration is annulled for the same two colours.

The distances  $c, d, f, g$  of the foci for  $C, D, F, G$  from the back of the last lens are given in the following table, for five zones of the objective, from direct trigonometrical calculation. The zones (infinitely narrow) are at the distances 0, 12.5, 17.68, 21.65, 25 mm. from the axis:

Distance from axis.	$c$	$d$	$f$	$g$
0 mm.	460.556 mm.	460.235 mm.	460.053 mm.	460.533 mm.
12.5	.560	.237	.063	.534
17.68	.577	.247	.072	.546
21.65	.598	.263	.083	.557
25	.621	.276	.094	.569

<sup>1</sup> The spectroscopie is indebted to improved glass-making, not only for well-corrected achromatic objectives, but also for prisms of high index and dispersion with relatively high transparency for visual and chemical rays.

In each column the numbers increase, but only very slightly, as we pass from the centre to the circumferential zone; the spherical aberration is therefore slightly overcorrected for all colours from *C* to *G*. This practically means that spherical aberration is annulled for the visual rays.

In fig. 16, which is drawn on the same scale as fig. 15, the focal curve for the central zone is marked *a*, and that for the

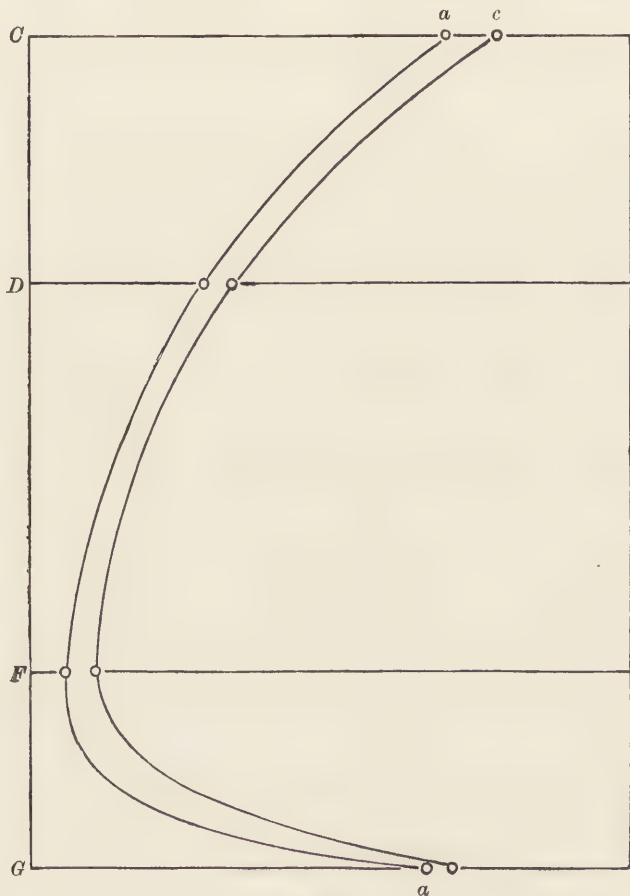


FIG. 16.

circumferential zone *c*; the curves for the intermediate zones lie between these two. The length of the secondary spectrum for the central zone is 0.503 mm.; and spherical aberration



increases the length by 0.065 mm. (or 13 per cent.), making it 0.568; which is at the rate of 1.23 mm. per metre of focal length.

**66. Objectives by Zeiss.** Our quotation from Wolf's report (Art. 63) may be supplemented by the following information taken from Zeiss' 1899 catalogue of astronomical objectives.

The astronomical department, which is under M. Pauly, has regarded the abolition of the secondary spectrum as its most important problem. For this purpose, new silicate glasses of proved durability have been produced. The similarity attained in run of dispersion between crown and flint, for the region *C* to *F*, has been such as to reduce the secondary spectrum to a minute remnant, so far as the visual range is concerned.

A second aim has been, to select, from the existing types of glass, such as would permit an increase of aperture ratio.

The following items from the catalogue originated at the Jena works; that is, were either invented there, or first made there in their present shape.

**Doublet Apochromatic Objectives**, without secondary spectrum, from new glasses of recent years. The crown employed cannot always be produced quite free from streakiness; but the little that remains has no influence on the sharpness of images. The aperture ratio is from 1/17 to 1/20.

The objectives are generally made with clear aperture 50-450 mm. and focal length 85-900 cm.

**Three-part Apochromatic Objectives** (König's) of one flint and two crowns; giving no secondary spectrum.

Aperture ratio, 1/10 to 1/15.

Clear aperture, 40-180 mm.

Focal length, 40-270 cm.

**Two-part Telescopic Objectives**, with secondary spectrum.

Aperture ratio, to 1/7.

Clear aperture, 60-200 mm.

Focal length, 42-200 cm.

**Three-part Telescopic Objectives**, with secondary spectrum.Aperture ratio,  $1/4$  to  $1/6$ .

Clear aperture, 20-150 mm.

Focal length, 8-90 cm.

**Apochromatic Aplanats** (Harting's) for astrophotography, without secondary spectrum; field about  $15^\circ$ ; of newly introduced glasses.

Aperture ratio, to  $1/8$ .

Clear aperture, 60-180 mm.

Focal length, 54-304 cm.

## CHAPTER VII.

### MECHANICAL PROPERTIES OF GLASS.

67. The **Density**, **Strength**, and **Elasticity** of glass have been investigated by Winkelmann and Schott.<sup>1</sup> Their experiments were performed upon 72 different kinds of glass; but in the system of numbering which they employ, 13 glasses are doubly and 3 glasses triply numbered, making 91 numbers in all. In the following table these numbers are given in the columns headed W. The left-hand portion of the table shows

W.	Trade No.	W.	Trade No.	W.	Trade No.	W.	W.
1	S. 185	25	O. 709	59	63 <sup>III</sup>	19	5
2	S. 205	26	O. 1571	60	O. 1022	22	2
3	172 <sup>III</sup>	33	O. 500	61	81 <sup>III</sup>	29	8
4	164 <sup>III</sup>	36	59 <sup>III</sup>	62	73 <sup>III</sup>	30	10
5	802	42	O. 428	63	93 <sup>III</sup>	31	13
6	16 <sup>III</sup>	43	458	64	90 <sup>III</sup>	35	7
7	165 <sup>III</sup>	46	O. 479	65	82 <sup>III</sup>	37	12
8	1419	47	O. 2154	66	87 <sup>III</sup>	38	6
9	S. 201	48	O. 885	67	83 <sup>III</sup>	39	11
10	290	49	O. 627	68	102 <sup>III</sup>	40	12
11	665	50	O. 165	69	S. 226	41	21
12	121 <sup>III</sup>	51	16 <sup>III</sup>	83	O. 137	44	36
13	S. 206	52	O. 55			45	2
14	S. 95	53	S. 41			51	6
15	1442	54	O. 527			53	13
16	S. 120	55	O. 1168			58	20
17	O. 331	56	O. 662			71	27
18	S. 163	57	S. 139			75	23
21	O. 658	58	S. 57			80	5

<sup>1</sup> See the four following Papers, which we shall quote as W., I.; W. and S., I.; W. and S., II.; W., II.

1. A. Winkelmann. On the specific heats of glasses of various compositions. *Ann. d. Phys. und Chem.*, 49, 401 (1893).

2. A. Winkelmann and O. Schott. On the elasticity and the tensional and compressive strength of various new glasses, in their relation to chemical composition; *l.c.* 51, 697 (1894).

3. A. Winkelmann and O. Schott. On thermal resistance-coefficients of various glasses in their relation to chemical composition; *l.c.* 51, 730 (1894).

4. A. Winkelmann. On the coefficients of elasticity of glasses of various compositions, and their dependence on temperature; *l.c.* 61, 105 (1897).

the corresponding trade numbers of 50 of the glasses; and the right-hand portion is a list of duplicate numbers (including the triplicates 2, 5, and 13).

For convenience of reference, we subjoin a complete table of the compositions of the 72 glasses.

W.	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	ZnO	PbO	MgO	Al <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>5</sub>	BaO	Na <sub>2</sub> O	K <sub>2</sub> O	Li <sub>2</sub> O	CaO	P <sub>2</sub> O <sub>5</sub>	Mn <sub>2</sub> O <sub>3</sub>
1	—	71.8	—	—	—	22.4	—	—	—	—	5.8	—	—	—
2	—	69.1	—	—	—	18.0	0.2	4.7	8.0	—	—	—	—	—
3	64.4	12.0	—	—	11.0	4.5	—	—	8.0	—	—	—	—	0.1
4	55.0	—	—	—	—	17.0	—	—	14.0	14.0	—	—	—	—
5	71.0	14.0	—	—	—	5.0	—	—	10.0	—	—	—	—	—
6	67.3	2.0	7.0	—	—	2.5	—	—	14.0	—	—	7.0	—	0.2
7	73.8	—	5.0	—	—	3.5	—	—	10.5	—	—	7.0	—	0.2
8	67.9	—	5.8	8.1	—	1.0	0.3	—	16.8	—	—	—	—	0.1
9	—	3.0	—	—	4.0	10.0	0.5	—	—	12.0	—	—	70.4	—
10	58.7	—	—	—	—	—	0.3	—	—	33.0	—	8.0	—	—
11	—	41.0	59.0	—	—	—	—	—	—	—	—	—	—	—
12	51.3	14.0	5.0	—	—	4.5	0.2	25.0	—	—	—	—	—	—
13	—	3.0	—	—	—	8.0	1.5	28.0	—	—	—	—	59.4	—
14	—	3.0	—	—	—	1.5	1.5	38	—	—	—	—	56.4	—
15	34.2	10.2	7.8	—	—	5.0	0.7	42.1	—	—	—	—	—	—
16	—	42.8	—	52.0	—	5.0	0.2	—	—	—	—	—	—	—
17	45.22	—	—	46.0	—	—	0.2	—	1.0	7.5	—	—	—	0.08
18	22.0	—	—	78.0	—	—	—	—	—	—	—	—	—	—
20	20.0	—	—	80.0	—	—	—	—	—	—	—	—	—	—
21	32.75	31.0	—	25.0	—	7.0	0.25	—	1.0	3.0	—	—	—	—
23	34.5	10.1	7.8	—	—	5.0	0.5	42.0	—	—	—	—	—	0.1
24	44.2	—	—	47.0	—	—	0.2	—	0.5	8.0	—	—	—	0.1
25	70.6	—	12.0	—	—	—	0.4	—	17.0	—	—	—	—	—
26	41.0	—	—	51.7	—	—	0.2	—	—	7.0	—	—	—	0.1
27	—	3.0	—	—	4.0	10.0	1.5	—	—	12.0	—	—	69.4	—
28	64.6	2.7	2.0	—	—	—	0.4	10.2	5.0	15.0	—	—	—	0.1
32	54.8	—	17.0	—	—	—	0.2	—	—	28.0	—	—	—	—
33	29.3	—	—	67.5	—	—	0.2	—	—	3.0	—	—	—	—
34	70.2	12.0	—	—	3.0	4.5	—	—	10.3	—	—	—	—	—
36	72.0	12.0	—	—	—	5.0	—	—	11.0	—	—	—	—	—
42	—	56.0	—	32.0	—	12.0	—	—	—	—	—	—	—	—
43	—	64.0	—	—	—	30.0	—	—	—	—	6.0	—	—	—
46	45.2	—	—	46.4	—	0.5	0.2	—	0.2	7.5	—	—	—	—
47	54.3	1.5	—	33.0	—	—	0.2	—	3.0	8.0	—	—	—	—
48	48.8	3.0	10.3	—	—	—	0.4	29.0	1.0	7.5	—	—	—	—
49	68.3	10.0	2.0	—	—	—	0.2	—	10.0	9.5	—	—	—	—
50	28.4	—	—	69.0	—	—	0.1	—	—	2.5	—	—	—	—
52	69.1	2.5	—	—	—	—	0.4	—	4.0	16.0	—	8.0	—	—
54	51.7	—	7.0	10.0	—	—	0.3	20.0	1.5	9.5	—	—	—	—
55	68.2	—	2.0	13.1	—	—	0.2	—	16.5	—	—	—	—	—
56	68.1	3.5	7.0	—	—	—	0.4	—	5.0	16.0	—	—	—	—
57	—	3.0	—	—	4.0	10.0	0.5	—	—	12.0	—	—	70.4	—
59	73.2	—	—	—	—	—	0.3	—	18.5	—	—	8.0	—	—
60	65.5	2.5	2.0	—	—	—	0.4	9.6	5.0	15.0	—	—	—	—
61	64.3	—	—	—	—	1.5	0.2	—	3.0	20.0	—	11.0	—	—
62	71.7	—	—	—	—	2.0	0.3	—	10.0	13.0	—	3.0	—	—
63	54.8	—	—	25.0	—	2.5	0.2	—	6.0	11.5	—	—	—	—



W.	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	ZnO	PbO	MgO	Al <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>3</sub>	BaO	Na <sub>2</sub> O	K <sub>2</sub> O	Li <sub>2</sub> O	CaO	P <sub>2</sub> O <sub>5</sub>	Mn <sub>2</sub> O <sub>3</sub>
64	69.7	—	—	—	—	—	0.3	—	—	25.0	—	5.0	—	—
65	64.3	—	—	—	—	2.5	0.2	—	9.0	15.0	—	9.0	—	—
66	58.8	—	8.0	6.0	—	4.0	0.2	—	10.0	14.0	—	—	—	—
67	43.0	—	—	34.0	—	4.0	—	—	8.0	11.0	—	—	—	—
68	57.0	—	5.0	—	—	12.0	—	—	13.0	13.0	—	—	—	—
69	21.0	—	—	79.0	—	—	—	—	—	—	—	—	—	—
70	51.0	—	12.0	—	—	—	—	5.0	—	32.0	—	—	—	—
72	45.1	—	—	46.4	—	—	—	—	0.5	0.8	—	—	—	—
73	—	68.8	—	—	—	18.0	—	5.0	8.0	—	—	—	—	—
74	4.0	54.5	12.0	11.5	—	14.0	—	—	—	4.0	—	—	—	—
76	26.5	29.0	—	34.0	—	9.0	—	—	0.5	1.0	—	—	—	—
77	65.9	2.5	2.0	—	—	—	—	9.6	5.0	15.0	—	—	—	—
78	67.4	—	3.6	13.0	—	—	—	—	16.0	—	—	—	—	—
79	71.0	—	12.0	—	—	—	—	—	17.0	—	—	—	—	—
81	67.9	—	5.8	8.0	—	1.0	0.3	—	16.8	—	—	—	—	—
82	61.6	—	—	—	—	15.0	0.3	—	23.0	—	—	—	—	0.1
83	70.6	—	—	—	—	—	0.3	—	2.0	16.0	—	11.0	—	0.1
84	67.7	8.0	9.0	—	5.0	—	0.3	—	10.0	—	—	—	—	—
85	48.1	4.5	10.1	—	—	—	0.4	28.3	1.0	7.5	—	—	—	0.1
86	54.2	1.5	—	33.0	—	—	0.2	—	3.0	8.0	—	—	—	0.1
87	68.2	10.0	2.0	—	—	—	0.2	—	10.0	9.5	—	—	—	—
88	70.4	7.5	—	—	—	—	0.2	—	5.3	14.5	—	2.0	—	0.1
89	69.0	2.5	—	—	—	—	0.5	—	4.0	16.0	—	8.0	—	—
90	69.5	2.0	—	2.5	—	2.5	0.4	—	7.0	16.0	—	—	—	—
91	74.6	—	—	—	—	—	0.3	—	9.0	11.0	—	5.0	—	0.1

**68. Density of Glass as dependent on Chemical Composition.** Let  $a_1, a_2, a_3 \dots$  denote the percentages of the several oxides of which a glass is composed, and  $z_1, z_2, z_3 \dots$  the densities to be attributed to them in the glass. Then, by adding the partial volumes, we have

$$\frac{a_1}{z_1} + \frac{a_2}{z_2} + \frac{a_3}{z_3} + \dots = \frac{100}{S}, \dots\dots\dots (1)$$

$S$  denoting the actual density of the glass. As might have been expected *a priori*, the quantities  $z_1, z_2, z_3 \dots$  are by no means identical with the densities of the separate oxides before combination. If these latter are put in place of  $z_1, z_2, z_3 \dots$ , they will give too small a value of  $S$ . The total volume is therefore diminished by the act of combination.<sup>1</sup>

The question arises whether one and the same oxide has always one and the same value of  $z$  in whatever mixture it occurs. If so, the values of  $z$  for the different oxides can easily be deduced from observations on properly selected glasses, and will enable us to compute the densities of other glasses, old or

<sup>1</sup> W. and S., II. 741.

new. This supposition is not rigorously fulfilled. Winkelmann and Schott have, however, shown<sup>1</sup> that the subjoined values for twelve of the oxides fulfil it approximately. When these values are employed to compute the densities of the 20 glasses numbered 19 to 38, neglecting the small amount of  $\text{Mn}_2\text{O}_3$  which some of them contain, the difference between computed and observed values is, on the average, only  $1\frac{1}{2}$  per cent., and amounts in only one case to 4 per cent.

Oxide	$z$	Oxide	$z$	Oxide	$z$	Oxide	$z$
$\text{SiO}_2$	=2.3	$\text{PbO}$	=9.6	$\text{As}_2\text{O}_5$	=4.1	$\text{K}_2\text{O}$	=2.8
$\text{B}_2\text{O}_3$	=1.9	$\text{MgO}$	=3.8	$\text{BaO}$	=7.0	$\text{CaO}$	=3.3
$\text{ZnO}$	=5.9	$\text{Al}_2\text{O}_3$	=4.1	$\text{Na}_2\text{O}$	=2.6	$\text{P}_2\text{O}_5$	=2.55

When we go outside these 20 glasses which were employed in determining the values of  $z$ , we find, in most cases, a fair agreement. The following list of observed and computed values includes, along with these 20 glasses, nine others whose densities are given in an earlier paper by Winkelmann.<sup>2</sup> Two of the latter

W.	Density.			W.	Density.		
	Obs.	Comp.	Obs.—Comp.		Obs.	Comp.	Obs.—Comp.
2=22	2.243	2.24	+ 0.1 %	20	5.944	5.87	+1.2 %
3	2.424	2.42	+ 0.2	21	2.758	2.75	+0.3
4	2.480	2.60	- 4.8	23	3.532	3.45	+2.3
5=19	2.370	2.31	+ 2.5	24	3.578	3.66	-2.2
6=38	2.585	2.52	+ 2.5	25	2.572	2.54	+1.2
7=35	2.479	2.50	- 0.8	26	3.879	3.88	-0.0
8=29	2.629	2.62	+ 0.3	27	2.588	2.52	+2.6
9	2.588	2.69	- 3.9	28	2.580	2.57	+0.4
10=30	2.518	2.51	- 0.3	32	2.668	2.75	-3.1
11	3.527	3.17	+10.1	33	4.731	4.78	-1.0
12=37	2.848	2.84	+ 0.3	34	2.378	2.34	+1.6
13=31	3.070	3.20	- 4.2	36	2.370	2.32	+2.1
14	3.238	3.37	- 4.1				
15	3.532	3.47	+ 1.8				
16	3.691	3.42	+ 7.3				
17	3.578	3.63	- 1.5				
18	5.831	5.65	+ 3.1				

<sup>1</sup> *l.c.* 739.<sup>2</sup> *W.*, I. 418.

—the zinc borate No. 11 and the lead borate No. 16—exhibit large discrepancies. Water at 4° is taken as the unit of density.

As the values of  $z$  for the glass-forming oxides are thus approximately constant over a wide range of composition, it is natural to compare them with the densities of the oxides before combination. The quotient of the former by the latter is given under the heading "Condensation" in the following list :

	Density.	Condensation.
BaO	5.00	1.400
B <sub>2</sub> O <sub>3</sub>	1.46	1.301
MgO	3.40	1.118
P <sub>2</sub> O <sub>5</sub>	2.38	1.071
Al <sub>2</sub> O <sub>3</sub>	3.85	1.065
SiO <sub>2</sub>	2.17	1.060
K <sub>2</sub> O	2.66	1.053
CaO	3.15	1.048
ZnO	5.65	1.044
PbO	9.32	1.030
Na <sub>2</sub> O	2.55	1.020
As <sub>2</sub> O <sub>5</sub>	4.09	1.002

Barium-oxide shows the largest increase of density (40 per cent.), and arsenic pentoxide the smallest (0.2 per cent.).

**69. The Tenacity** (tensile strength) was determined by Winkelmann and Schott for 17 glasses, numbered 19 to 35 in Winkelmann's series; the specimens being square rods, of cross-sections ranging from 11.55 to 19.27 mm. The apparatus employed was modelled on that used by W. Voigt and A. Sella for observations on rock salt;<sup>1</sup> but the load (which often exceeded 100 kg.) was applied, not by means of flowing mercury, but by weights, and it was necessary to employ an "arrester," by the lowering or raising of which the load could be put on or off. The distance fallen through when rupture occurred was only 0.5 mm. Half way up the rod, a shallow depression running all round it was produced by means of a grinding tool of cylindrical form, and was afterwards polished. As a result of this arrangement, combined with precautions for ensuring a central pull, surfaces of rupture were obtained, which showed,

<sup>1</sup> Göttinger Nachrichten, No. 14, p. 494 (1892).

over nearly their whole area, the dull fibrous appearance indicative of tearing. The load was kept on for not more than 40 seconds. If rupture did not occur, the arrester was raised till it took off the load; and the load was then increased by from 1 to 3 kg., and the arrester slowly lowered. This process was repeated till rupture occurred. The following table gives for each kind of glass the number of observations, the minimum, the mean, and the maximum.

W.	No. of Obs.	Tenacity in kg/mm <sup>2</sup>			Calculated.	Obs.—Calc.
		Observed.				
		Min.	Mean	Max.		
19=5	5	6.51	6.76	6.95	7.75	- 11 %
20	4	2.90	3.28	3.53	3.80	- 8
21	9	5.18	5.66	6.12	5.99	+ 2
22=2	5	4.58	4.93	5.76	5.79	- 1
23	6	6.78	7.21	7.52	7.30	+ 3
24	2	5.95	6.01	6.07	5.26	+13
25	5	7.00	7.84	8.51	8.51	± 0
26	5	4.25	4.67	5.39	5.06	+ 6
27	2	5.36	5.46	5.56	6.11	-10
28	3	5.60	6.09	6.76	7.07	- 5
29=8	4	6.00	6.42	6.79	7.59	-12
30=10	3	7.02	7.52	7.82	7.22	+ 8
31=13	5	7.06	7.42	7.63	6.50	+15
32	3	7.87	8.09	8.32	7.75	+ 7
33	4	4.65	4.97	5.32	4.36	+18
34	3	7.66	7.92	8.16	7.56	+ 7
35=7	4	6.62	7.46	8.35	9.19	-10

The errors in these observations arise partly from imperfect centring of the rods, and partly from superficial inequalities of condition, causing rupture to begin at a place of small resistance. Both sources of error make the result too small. We shall therefore adopt the maximum value as probably nearest to the truth. In two instances (26 and 35), the minimum is smaller by 21 per cent.; and if we leave out of the calculation glasses 24 and 27, for each of which there are only two observations, the difference is always, except in the case of 32, much more than 5 per cent.



**Relation between Tenacity and Chemical Composition.**

The attempt was made to express the tenacity  $P$  by the formula

$$P = a_1y_1 + a_2y_2 + a_3y_3 + \dots,$$

$a_1, a_2, a_3, \dots$  denoting the percentages of the several oxides in the total composition. The values adopted for  $y$  were:

$y$	$y$	$y$	$y$
SiO <sub>2</sub> = 0.09	PbO = 0.025	As <sub>2</sub> O <sub>5</sub> = 0.03	K <sub>2</sub> O = 0.01
B <sub>2</sub> O <sub>3</sub> = 0.065	MgO = 0.01	BaO = 0.05	CaO = 0.20
ZnO = 0.15	Al <sub>2</sub> O <sub>3</sub> = 0.05	Na <sub>2</sub> O = 0.02	P <sub>2</sub> O <sub>5</sub> = 0.075

and by employing these, the values in the column headed "Calculated" were obtained. The differences between these calculated values and the observed maxima are, on the average, 8 per cent. The order of the oxides, when arranged according to the values of  $y$ , beginning with the largest, is: CaO, ZnO, SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, B<sub>2</sub>O<sub>3</sub>, BaO, Al<sub>2</sub>O<sub>3</sub>, As<sub>2</sub>O<sub>5</sub>, PbO, Na<sub>2</sub>O, K<sub>2</sub>O, MgO. Those which stand first exert a favourable, those which stand last an unfavourable influence on tenacity. Some uncertainty attaches to the positions of CaO, As<sub>2</sub>O<sub>5</sub>, and MgO in the list, owing to the small proportions of these oxides contained in the glasses in question. The quantity of Mn<sub>2</sub>O<sub>3</sub> is so minute that no value of  $y$  has been assigned to it.

**70. Resistance to Crushing.** As a sequel to the observations on tenacity, Winkelmann and Schott have investigated the resistance to crushing for the same 17 glasses, 19-35.<sup>1</sup> The force was applied by means of a press filled with oil, in which the pressure could be gradually increased by screwing in a screw-plunger. The attached manometer indicated forces up to 50 kg. The specimens of glass tested were approximately cubes of 6 mm. edge, and were squeezed between two metal plates with gradually increasing pressure, till they flew into powder. The rupture occurred suddenly, with a loud report, and a flash of light clearly seen in the dark. Preliminary trials showed that the greater or less hardness of the metal plates largely influenced the results. Glass 19 between tin plates showed, in three experiments, a mean resistance of 39.2 kg. per sq. mm. Between copper plates, it showed, in four experiments, a mean of 65.8. The tin

<sup>1</sup> W. u. S., I. 720.

plates, when examined, showed deep depressions, in which linear elevations were noticeable. The metal had evidently been forced into small cracks produced in the glass by the pressure. The copper plates also showed the small elevations in the deep depressions, but not so distinctly as the tin plates.

After this experience, hard steel plates 5 cm. square and 1.5 cm. thick were employed. They were carefully ground smooth, and the glass was crushed between them. Even in these plates depressions were produced by the strongest glasses, necessitating frequent regrinding. Experiments made for the purpose showed that damaged surfaces gave too low values of resisting power. The following table shows for each glass the number of observations and their mean.

W.	No. of Obs.	Resistance to Crushing in kg/mm <sup>2</sup>		Obs.-Calc.	Ratio to Tenacity.	
		Obs.	Calculated		a	b
19=5	4	126.4	110.9	+12 %	18.7	18.2
20	4	60.6	63.0	- 4	18.5	17.2
21	4	105.7	88.2	+17	18.7	17.3
22=2	5	81.2	88.1	- 8	16.5	14.1
23	9	84.0	87.8	- 5	11.7	11.2
24	5	77.5	77.9	- 1	12.9	12.8
25	4	97.8	104.6	- 7	12.5	11.5
26	4	84.3	75.8	+10	18.1	15.6
27	4	71.7	72.0	- 0	13.1	12.9
28	3	91.6	93.7	- 2	15.0	13.6
29=8	5	99.0	102.3	- 3	15.4	14.6
30=10	4	68.3	75.7	-11	9.1	8.7
31=13	3	75.0	74.8	+ 0	10.1	9.8
32	6	73.9	79.2	- 7	9.1	8.9
33	4	67.3	68.8	- 2	13.5	12.7
34	5	99.3	111.1	-12	12.5	12.2
35=7	4	112.9	105.2	+ 7	15.1	13.5

The results for one and the same glass often exhibited large differences. In the cases of 23 and 29, the minimum was about 26 per cent. below the maximum.

Glass 19 was also tried in smaller cubes of 4.5 mm. in the edge, and gave a mean resistance of 115.3 kg. per sq. mm. It would therefore seem that the resistance per sq. mm. increases

somewhat as the section increases. The observations in the table nearly all relate to sections not very different from 36 sq. mm. For glass 35 it was, however, 45 sq. mm., and for glass 34 it was 50 sq. mm. The comparability of the results is thus sufficiently exact.

Five other substances were tested in the same way, for the sake of comparison with the glasses, and gave the following resistances to crushing:

Black Belgian marble,	-	-	-	25.4 kg. per mm <sup>2</sup> .
White Italian marble,	-	-	-	7.1
Saxon granite, -	-	-	-	19.1
Brazilian agate,	-	-	-	131.7
Rock crystal	{	pressure parallel to axis,		- 181.6
		,, perpendicular,,		- 160.0

Cast iron, similarly treated, did not go to pieces. When the pressure per sq. mm. exceeded 94.1, its sectional area was increased, and this prevented increase of intensity of pressure.

**Relation between Resistance to Crushing and Chemical Composition.** The values in the column headed "Calculated" were obtained by employing a linear formula (as in the case of tenacity), with the following values of  $y$ :

$y$	$y$	$y$	$y$
$\text{SiO}_2 = 1.23$	$\text{PbO} = 0.48$	$\text{As}_2\text{O}_5 = 1.0$	$\text{K}_2\text{O} = 0.05$
$\text{B}_2\text{O}_3 = 0.9$	$\text{MgO} = 1.1$	$\text{BaO} = 0.05$	$\text{CaO} = 0.2$
$\text{ZnO} = 0.6$	$\text{Al}_2\text{O}_3 = 1.0$	$\text{Na}_2\text{O} = 0.02$	$\text{P}_2\text{O}_5 = 0.76$

The next column gives the differences between the calculated and observed values, as percentages of the observed. The average difference is 6.4, and the greatest 17 per cent. The arrangement in descending order of  $y$  is:  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{As}_2\text{O}_5$ ,  $\text{B}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{BaO}$ ,  $\text{ZnO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{PbO}$ ,  $\text{CaO}$ ,  $\text{K}_2\text{O}$ .

**The Ratio to Tenacity** is given by two different modes of comparison. Column a shows the ratio of the mean values of the two kinds of resistance; column b the ratio of the mean value of resistance to crushing to the maximum value of tenacity. Glasses of different composition exhibit very different ratios.

**71. The few Earlier Observations on the Strength of Glass** which are available are not accompanied by any informa-

tion as to the chemical composition of the glasses to which they relate.<sup>1</sup> For the sake of comparison, we will adduce the observations of J. v. Kowalski.<sup>2</sup> They were made on thin glass rods, "drawn from a melting which was free from bubbles, and then slowly and carefully cooled." Their section was found to be approximately an ellipse, with very small difference between its two axes. In a series of 30 experiments on tenacity, the maximum obtained was 8·981 kg. per sq. mm., the minimum 8·628, and the mean 8·767. In 14 experiments on resistance to crushing, the maximum did not exceed 42·063, and the mean was only 37·700. The circumstance "that v. Kowalski, in investigating resistance to crushing, placed the glass rods between two copper plates, does not seem sufficient to explain the smallness of his values. The explanation is rather to be found in the fact that he appears to have only carried his pressure to the point at which the first fracture parallel to the direction of pressure occurred; this being far below the pressure which would have produced complete disintegration."<sup>3</sup>

Observations were also made by v. Kowalski on the resistance of glass rods to flexure and torsion. From 29 observations on flexure, it was inferred that the tension on the convex side of the bent rod had the mean value 8·794 kg. per sq. mm. Strength to resist torsion was tested by 33 experiments. The greatest tension occurs at the ends of the axis minor of the elliptic section, and is inclined at 45° to the length of the rod. The mean value found for this greatest tension was 10·142. Finally, for each kind of test the greatest linear extension was calculated. In the experiments on direct pull, this was in the direction of the length. When the rod is supported on two knife-edges and loaded in the middle, the greatest extension is at the lowest point, and is parallel to the length. In torsion it has the direction and position indicated above. Lastly, in end pressure, it is perpendicular to the pressure. The values found were:

In simple pull, -	-	-	-	0·00131
In bending, -	-	-	-	·00132
In torsion, -	-	-	-	·00183
In end pressure, -	-	-	-	·00129

<sup>1</sup> W. and Sch., I. 697 *et seq.*

<sup>2</sup> *Ann. d. Phys. u. Chem.*, 36, 307 (1887).

<sup>3</sup> W. and Sch., I. 727.



Hence it would appear that glass can bear a considerably greater extension by torsion than by pull or bending or end pressure.<sup>1</sup>

**Falling off of Strength at Higher Temperature.** A later communication by v. Kowalski contains observations on the flexural and torsional strength of glass at higher temperatures.<sup>2</sup> The material was the same as in the previous experiments. The flexural experiments gave the following means, each derived from 18 observations:

Temp.	Greatest tension.	Greatest extension.
12°	8·794 kg./mm <sup>2</sup> .	0·00132
100	8·701	·00145
150	8·639	·00156
200	8·604	·00162

The torsional experiments gave the following means, each derived from 11 observations:

Temp.	Greatest tension.	Greatest extension.
12°	10·142 kg/mm <sup>2</sup> .	0·001837
78	9·182	·001872
100	9·006	·001901

**72. Young's Modulus of Elasticity.** The first systematic investigation of the elasticity of glass was made by Winkelmann and Schott,<sup>3</sup> who determined the values of this coefficient for 19 different kinds of glass, 19-29 and 31-38. In the case of the first 16 glasses, 19-29 and 31-35, the values were deduced from observations of flexure.

When a rod of rectangular section is supported on two fixed knife-edges and loaded in the middle, its two ends turn in opposite directions through the same angle  $\phi$ . If this angle is observed, the coefficient of elasticity  $E$  (Young's modulus) is given by the formula

$$E = \frac{3}{4} \frac{l^2}{a^3 b} \frac{P}{\tan \phi}, \dots\dots\dots (1)$$

$l$  denoting distance between knife-edges,  $a$  depth of section,  $b$  breadth of section, and  $P$  the load. For the determination

<sup>1</sup> The change in a small superficial element of a rod under torsion is a simple shear, which is made up of an extension in one direction and a compression in a perpendicular direction, each of these directions being inclined at 45° to the axis of the rod, and parallel to the tangent plane. The compression tends to prevent the rupture due to the extension.—J. D. E.

<sup>2</sup> *Ann. der Phys. u. Chem.*, 39, 155 (1890).

<sup>3</sup> *W. u. Sch.*, I. 700.

of  $\phi$ , the following method has been indicated by A. König.<sup>1</sup> The two ends of the rod carry two mirrors  $B, C$ , whose planes are nearly vertical, but face slightly upwards. A ray from a point  $E$

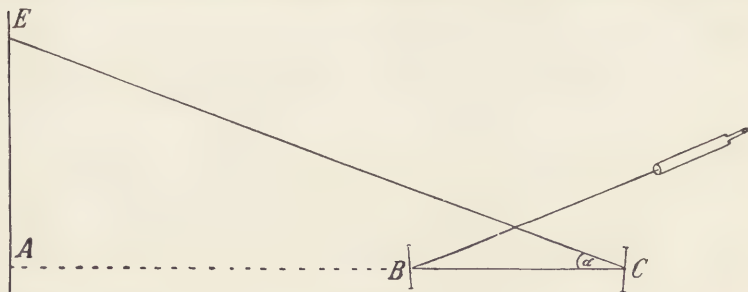


FIG. 17.

of a distant scale is reflected from  $C$  to  $B$ , and thence into an observing telescope. When the rod is bent by putting on the load, a displacement of the point  $E$  on the scale is observed in the telescope. Calling this displacement  $v$ , it can be shown that (putting  $D$  for  $AC$  and  $d$  for  $BC$ )

$$v = D \tan \alpha - D \tan(\alpha - 4\phi) + d \tan 2\phi, \dots\dots\dots(2)$$

$\alpha$  denoting the inclination of  $CE$  to the horizontal line  $CBA$ . Since  $4\phi$  is small, (2) can be written

$$v = 4\phi(D \sec^2 \alpha + \frac{1}{2}d); \dots\dots\dots(2A)$$

which, when  $\alpha$  is small, gives

$$v = 4\phi(D + \frac{1}{2}d); \dots\dots\dots(3)$$

and this, combined with (1), gives

$$E = 3(D + \frac{1}{2}d) \frac{l^2}{a^3 b} \frac{P}{v}. \dots\dots\dots(4)$$

This method of König's required a greater length of rod than was available for some of the glasses. It was accordingly modified on the plan sketched in fig. 18; the course of the twice

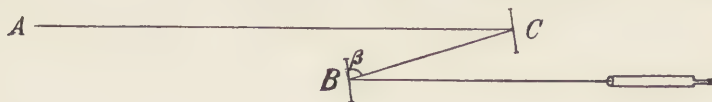


FIG. 18.

reflected ray being in a horizontal or nearly horizontal plane instead of in a vertical plane as in fig. 17. The effective rays

<sup>1</sup> *Ann. Phys. Chem.*, 28, 108 (1886); also Kohlrausch, *Prakt. Physik*, 35, II.; and Winkelmann, *Handb. d. Phys.*, I. 263.

from the point *A* of the scale passed just clear of the mirror *B* on their way to *C*. The two mirrors were approximately parallel, and their normals were inclined at about  $4^\circ$  to the incident and reflected rays. The angle marked  $\beta$  was therefore about  $86^\circ$ ; and this obliquity was allowed for by employing, in equation (3), the corrected value  $v/\sin \beta$  instead of the observed deflection  $v$ . Equation (4) was thus reduced to the modified form

$$E = 3 \left( D + \frac{d}{2} \right) \frac{l^2}{a^3 b} \frac{P}{v} \sin \beta. \dots\dots\dots (5)$$

The most important source of error is inexact measurement of the depth  $a$  of the cross section of the rod; for this factor occurs in the third power. It was measured, for each rod, in 15 places uniformly distributed over the surface, with the help of Abbe's callipers. In calculating the mean, double weight was assigned to the three measurements made at the middle of the rod. If we assume that, in cases in which the single measurements have differences of 0.1 mm., the calculated mean value of  $a$  is affected with an error of 0.2 mm., this will involve an error of 2 per cent. in the coefficient of elasticity, seeing that  $a$  is about 3 mm.

Of the three remaining glasses, 36, 37, 38, the first two could not be obtained in the form of rods, and were examined by Kundt's method for determining the velocity of sound.<sup>1</sup> The third (normal thermometer glass) was examined both by this method and by observations of flexure.

A second investigation was carried out by Winkelmann at a later date, its chief object being to ascertain how the elasticity alters with rising temperature. The first series of observations<sup>2</sup> were taken at ordinary temperatures, and are comparable with those mentioned above. They included 23 kinds of glass, namely 19-38, omitting 20, 24, 27, 36, 37; and in addition, 84-91. In the observations at higher temperatures, a different arrangement



FIG. 19.

was adopted, the two mirrors being replaced by two isosceles right-angled prisms, *C* and *B* (fig. 19) having their edges vertical. The ray from the scale at *A* is four times totally reflected in a

<sup>1</sup> Kohlrausch, *Prakt. Phys.*, 37.<sup>2</sup> W., II. 119.

horizontal plane, and the last part of its course is nearly parallel to the first. In the calculation of the elasticity, equation (4) is applicable, for  $a$  in (2) is zero.

The results of the two investigations are combined in the following table, under the headings  $E_1$ ,  $E_2$  respectively:

W.	$E_1$	$E_2$	W.	$E_1$	$E_2$
19=5	7296 kg/mm <sup>2</sup>	7563 kg/mm <sup>2</sup>	33	5512 kg/mm <sup>2</sup>	5477 kg/mm <sup>2</sup>
20	5088	—	34	7001	7180
21	5474	5468	35=7	7077	7314
22=2	4699	4906	36	7260	—
23	7952	7992	37=12	7232	—
24	5389	—	38=6	7340	7465
25	6498	6766	84	—	7401
26	5467	5461	85	—	7416
27	6780	—	86	—	6097
28	6626	6599	87	—	7971
29=8	6514	6638	88	—	7461
30=10	—	6014	89	—	7186
31=13	6296	6373	90	—	6338
32	5862	5843	91	—	6572

The dimensions of the rods are not stated in the table. For the columns headed  $E_1$  the depth  $a$  of the cross section was between 2.695 and 4.335 mm., and the breadth  $b$  between 9.269 and 16.384 mm. The means were (in round numbers)  $a = 3$  mm.,  $b = 15$  mm. For the rods to which the columns  $E_2$  relate,  $a$  was between 3.176 and 4.044 mm.,  $b$  between 8.484 and 16.091 mm. The means in round numbers were  $a = 3.5$  and  $b = 15$  mm.

In several instances, the values under  $E_1$  and  $E_2$  for one and the same glass differ considerably. These differences are explained by the following considerations:

It is not improbable that the uncertainty in the value of  $a$  may produce a maximum error of 2 per cent.

The glass 19 was from two different meltings in the two cases, and it is possible that its actual composition was slightly different, especially as regards boric acid. The glass 22 was also from two different meltings. Glasses 34 and 35 showed the presence of stresses, and these have a considerable influence on elasticity. Glass 38 contained layers of bubbles, and therefore was not completely homogeneous.



**Dependence of Elasticity on Chemical Composition.** The attempt was made, as in the case of other properties previously mentioned, to express the elasticity (Young's modulus) by the formula

$$E = a_1x_1 + a_2x_2 + a_3x_3 + \text{etc.},$$

$a_1, a_2, a_3 \dots$  being the percentages of the several ingredients of the glass. It was found that the 19 values given under the heading  $E_1$  were represented in a satisfactory way by giving  $x$  the following values:<sup>1</sup>

$x$	$x$	$x$	$x$
SiO <sub>2</sub> = 65	PbO = 47	As <sub>2</sub> O <sub>5</sub> = 40	K <sub>2</sub> O = 71
B <sub>2</sub> O <sub>3</sub> = 20	MgO = 600	BaO = 100	CaO = 100
ZnO = 15	Al <sub>2</sub> O <sub>3</sub> = 160	Na <sub>2</sub> O = 100	P <sub>2</sub> O <sub>5</sub> = 38

The attempt to calculate the elasticities of the additional glasses included in the second series, by the use of these numbers, was not very successful.

In order to obtain satisfactory agreement between formulae and observed elasticities for all the glasses examined, Winkelmann<sup>2</sup> divides them into three groups: A, B, C. Group A comprises the pure silicate glasses, which contain neither boric acid nor phosphoric acid, and are also free from baryta and magnesia. Group B contains the lead-free borosilicates; they are also free from phosphoric acid. Group C is composed of the remaining glasses, comprising borates, lead borosilicates, and phosphates. The corresponding values of  $x$  are given in the following table:

	Values of $x$ for the group.		
	A	B	C
SiO <sub>2</sub>	70	70	70
B <sub>2</sub> O <sub>3</sub>	—	60	25
ZnO	52	100	—
PbO	46	—	55
MgO	—	40	30
Al <sub>2</sub> O <sub>3</sub>	180	150	130
As <sub>2</sub> O <sub>5</sub>	40	40	40
BaO	—	70	30
Na <sub>2</sub> O	61	100	70
K <sub>2</sub> O	40	70	30
CaO	70	70	—
P <sub>2</sub> O <sub>5</sub>	—	—	70

<sup>1</sup> W. u. Sch., I. 711.<sup>2</sup> W., II. 122.

The values of Young's modulus, calculated by the help of these numbers, are given side by side with the observed values in the following table:

	Elasticity in kg per mm <sup>2</sup>		
	Observed.	Calculated.	Obs.-Calc.
Group A			
20	5088	5080	+0 %
24	5389	5614	-4
25	6632	6619	+0
26	5464	5536	-1
29=8	6576	6644	-1
30=10	6014	6001	+0
32	5852	5848	+0
33	5494	5284	+4
35=7	7195	7186	+0
91	6572	6573	-0
Group B			
19=5	7563	7560	+0
23	7972	7511	+6
28	6613	7164	-8
34	7090	7459	-5
36	7260	7610	-5
37=12	7232	7364	-2
38=6	7402	7796	-4
84	7401	7331	+1
85	7416	7269	+2
87	7971	7247	+9
88	7461	7071	+5
89	7186	7080	+1
Group C			
21	5471	5521	-1
22=2	4802	4776	+1
27	6780	6780	0
31=13	6334	6180	+2
86	6097	6104	-0
90	6338	6363	-0

**73. Elasticity of Glass at Higher Temperatures.** As already stated, Winkelmann extended his observations on glass rods to higher temperatures.<sup>1</sup> Of the 28 glasses mentioned in

<sup>1</sup> W., II.

the preceding article, 24 were subjected to this further test, the four omitted being 20, 27, 36, 37. The determinations were carried as far as the temperatures at which the glasses began to be plastic, that is, in the case of the least fusible, to nearly  $500^{\circ}$ .

For these new observations, the apparatus previously used was enclosed in a metal case, consisting of several boxes one within another, and covered externally with asbestos. Two brass tubes, closed at the ends by glass plates, were screwed into the walls so as to give a view through the centre. The case was heated by a ring of eight Bunsen burners, and the gases from the flames streamed through the interspace between the walls. The temperatures were indicated by two thermometers going through the top walls of the case. They were of borosilicate glass 59<sup>III</sup>, and had been tested at the Reichsanstalt. The lower parts of their tubes were graduated from  $-10^{\circ}$  to  $+10^{\circ}$ . Then followed a widening, and then a graduation from  $180^{\circ}$  to  $550^{\circ}$ . The portion from  $200^{\circ}$  downwards was within the case, and an auxiliary thermometer gave the temperature of the external portion of the mercurial column.

The ordinary silver-covered mirrors soon gave hazy images, in consequence of the heat to which they were exposed, and after a little while became quite useless. Their place was therefore supplied by two right-angled isosceles prisms, arranged as in fig. 19. Very few kinds of glass were suitable either for the prisms or the window plates; most kinds becoming dull and softening at the high temperatures which were employed. The heavy baryta glass No. 23 proved the best, and was generally employed.

When the apparatus is set up as above described, and the observing telescope focussed on the scale, the scale is seen out of focus after the temperature has risen; and sharpness can be restored by moving the scale further away. Winkelmann traced this effect to the action of the heat on the window plates which closed the ends of the two metal tubes. The tubes, becoming heated by the flame-gases, communicated heat to the glass plates, which thus became hotter at the circumferences than at the centres. This difference of temperature acts in two ways. In the first place, it makes the plates thicker at the circumferences than at the centres, so that they are double-

concave instead of plane. In the second place, the index, being greater for hot glass than for cold, increases from the centre outwards.<sup>1</sup> Both actions make the plates act as diverging lenses (see Art. 29). Winkelmann shows, by calculation, that the differences of temperature which would be required, according to this explanation, to produce the effect actually observed, are not greater than it is reasonable to assume. The correctness of the explanation was also confirmed by experiments separately performed on one of the view-tubes.

If the flexure experiments at ordinary temperatures are first performed, no important after-effects are observed during their continuance or after their cessation. At high temperatures it is quite otherwise; the scale continues to move across the field of the telescope for some minutes after putting on or taking off the load. This made it necessary to employ an assistant, with a lever arrangement by which he could put the weight on or off in a fraction of a second, the observer remaining all the time at the telescope.

It was also necessary to attend to thermo-elastic after-effects. If a glass is first tested for elasticity at ordinary temperatures, and then raised to a high temperature, it exhibits, on its return to ordinary temperature, greater resistance to bending than before heating. If it only undergoes one such heating, the new and larger elasticity observed at ordinary temperatures changes in course of time. Several successive heatings and intervals of cooling are required before the elasticity becomes constant. In comparing elasticities at lower and higher temperatures, the heatings and coolings were continued to this point, and the constant results thus obtained were adopted.

**Statement of Results.** Out of the 24 glasses which were tested in the manner above described, only nine showed a linear relation between elasticity and temperature; in the rest elasticity diminished more quickly as the temperature rose. Winkelmann adopted, for the expression of his results, the formula

$$E_t = E_{20}[1 - \alpha(t - 20)^2]. \dots\dots\dots(1)$$

$E_t$  denoting the elasticity at  $t^\circ$ . Equation (4) of Art. 72 gives

<sup>1</sup>For glass 23, according to Reed's observations,  $n_D$  is 1.60982 at  $10^\circ$  and 1.61194 at  $404^\circ$ . Cf. Art. 28.



$E_t/E_{20} = v_{20}/v_t$ ; hence we have

$$\log a + \beta \log(t - 20) = \log\left(1 - \frac{v_{20}}{v_t}\right) \dots \dots \dots (2)$$

Substituting, in this equation, the values of the displacement  $v$  for  $20^\circ$  and for two suitably selected higher values of  $t$ , two equations are obtained, from which  $a$  and  $\beta$  can be determined. The following table contains the results for the 24 glasses; the first column containing Winkelmann's numerical designations of the glasses, and the last column the highest temperatures to which the glasses were heated; these being the temperatures employed in calculating the two constants.

W.	$E_{20}$	$\log a$	$\log \beta$	Highest Temperature.
19=5	7672 kg/mm <sup>2</sup>	0.01760 - 9	0.42810	482°
21	5606	0.45239 - 15	0.70586	383
22=2	5023	0.44871 - 4	0	281
23	8146	0.32998 - 5	0.09364	486
24	5433	0.89662 - 13	0.64253	413
25	6983	0.91177 - 5	0.06481	409
26	5505	0.49224 - 24	0.94544	340
28	6669	0.57519 - 4	0	394
29=8	6650	0.40100 - 15	0.71706	433
30=10	6159	0.69552 - 5	0.11280	455
31=13	6441	0.22967 - 6	0.25523	412
32	5885	0.19312 - 4	0	417
33	5494	0.63418 - 8	0.40114	357
34	7349	0.11394 - 5	0	482
35=7	7524	0.54267 - 5	0.08213	460
38=6	7649	0.43533 - 6	0.23175	426
84	7564	0.09160 - 11	0.55261	407
85	7589	0.92267 - 6	0.16550	427
86	6218	0.97275 - 10	0.49890	374
87	8340	0.24797 - 4	0	447
88	7551	0.35218 - 4	0	475
89	7234	0.36922 - 4	0	433
90	—	0.61595 - 4	0	434
91	6687	0.61805 - 4	0	448

From these values of  $\log a$  and  $\log \beta$ , Winkelmann deduced

the values of  $1 - E_t/E_{20}$  for certain values of  $t$ , as shown in the following table:

W.	$(1 - E_t/E_{20}) 100$				
	100°	200°	300°	400°	500°
19=5	0·01	0·11	0·38	0·85	1·95
21	0·00	0·08	0·76	3·61	—
22=2	2·25	5·06	7·87	—	—
23	0·49	1·34	2·32	3·39	4·53
24	0·02	0·63	4·37	16·60	—
25	1·32	3·38	5·66	8·07	—
26	0·00	0·02	1·18	—	—
28	3·01	6·77	10·53	14·29	—
29=8	0·00	0·14	1·44	7·05	—
30=10	1·45	4·16	7·39	10·97	14·86
31=13	0·45	1·94	4·31	7·46	—
32	1·25	2·81	4·37	5·93	—
33	0·27	2·06	6·27	—	—
34	0·10	0·23	0·36	0·49	0·62
35=7	0·69	1·85	3·16	4·57	6·06
38=6	0·50	1·91	4·17	6·82	—
84	0·01	0·14	0·67	2·00	—
85	0·51	1·67	3·20	5·01	—
86	0·09	1·22	4·92	—	—
87	1·42	3·19	4·96	6·73	—
88	1·80	4·05	6·30	8·55	10·80
89	1·87	4·21	6·55	8·89	—
90	3·30	7·43	11·56	15·69	—
91	3·32	7·47	11·62	15·76	—

For glass 22 containing 69·1 per cent. of boric acid, and for glasses 26, 33, 86 containing large proportions of lead oxide, no values are given at 400°, because this temperature was too high for them. At 500° results are given for only the six glasses—19, 23, 30, 34, 35, 88. Most glasses soften or are on the point of softening at this temperature.

**Remarks on the Results.** Write  $Q$  as an abbreviation for  $1 - E_t/E_{20}$ , so that equation (1) may be written

$$Q = \alpha(t - 20)^2 \dots\dots\dots (3)$$

For nine of the glasses  $\beta$  is unity, so that at all temperatures above  $20^\circ$  the glass of greater  $\alpha$  has also the greater  $Q$ . These glasses, arranged in ascending order of  $\alpha$ , are: 22, 28, 32, 34, 87, 88, 89, 90, 91.

As regards the influence of  $\beta$ , let two glasses have the same value of  $Q$  at a particular temperature  $\theta$ . Then, using the subscripts 1 and 2 to distinguish values for the two glasses, we find, from (3),

$$\log(\theta - 20) = \frac{\log \alpha_1 - \log \alpha_2}{\beta_2 - \beta_1}.$$

But (3) gives, by differentiation,

$$\frac{dQ}{dt} = \frac{\beta}{t - 20} Q;$$

hence, at the temperature  $\theta$  at which  $Q$  is the same for both, the glass which has the greater  $\beta$  has the greater  $dQ/dt$ . At higher temperatures this glass will have the greater  $Q$ , and at lower temperatures the smaller  $Q$ .

**Influence of Chemical Composition.** No satisfactory results have been obtained in the attempt to express  $\alpha$  and  $\beta$  as linear functions of the percentages of the several constituents. Taking, first, the glasses for which  $\beta$  is unity, so that greater  $\alpha$  means more rapid diminution of elasticity with rise of temperature; if we exclude the borate glass 22 and arrange the others in order of ascending  $\alpha$ , the last six of the series are borosilicates in which potash and soda are both present, namely, 87, 88, 89, 28, 90, 91. Taking account of their varying percentages of boric acid, Winkelmann suggests that the simultaneous presence of large amounts of soda and potash favours the change of elasticity with temperature, but that the presence of boric acid along with them tends in the opposite direction.<sup>1</sup>

If the 15 glasses for which  $\beta$  is not unity are arranged in ascending order of  $\beta$ , the series is: 25, 35, 23, 30, 85, 38, 31, 33, 19, 86, 84, 24, 21, 29, 26. If arranged in descending order of  $\alpha$ , the order is the same, except that glass 30 is second instead of fourth. This order of succession does not correspond to any regular order of chemical composition; for example, the only phosphate is number 31. The glasses which contain lead have

<sup>1</sup> W. II., 131.

certainly the largest values of  $\beta$ , but not in the order of their amounts of lead; for this would give the order: 29, 21, 86, 24, 26, 33. Glass 90 is exceptional, for its  $\beta$  is unity; but it only contains 2.5 per cent. of lead.

**74. Correction to be made for Thermal Expansion.** Thus far the linear measurements  $a, b, l$  in the expression (4) for the elasticity (Art. 72) have been treated as constant; but they in fact change with temperature. Writing  $E'$  for corrected and  $E$  as before for uncorrected values, we have

$$\frac{E'_t}{E'_0} = \frac{E_t}{E_0} \cdot \frac{l_t^2}{l_0^2} \cdot \frac{a_0^3 b_0}{a_t^3 b_t} \dots\dots\dots (1)$$

The supporting knife-edges, whose distance is  $l$ , were portions of a massive apparatus of brass;  $a$  and  $b$  are the depth and width of the glass rod. If  $\alpha$  denote the coefficient of linear expansion for brass, and  $\beta$  for glass, equation (1) gives, to the first order of small quantities,

$$\frac{E'_t}{E'_0} = \frac{E_t}{E_0} [1 + (2\alpha - 4\beta)t]. \dots\dots\dots (2)$$

According to the observations of Le Chatelier,<sup>1</sup> the mean value of  $\alpha$  between 0° and 40° is 0.0000186, and between 0° and 700° 0.0000225.

Assuming that the mean value of  $\alpha$  from 0° to  $t^\circ$  is of the form  $A + Bt$ , we deduce:

	Mean $\times 10^7$ .
0° to 100°,	190
200,	195
300,	201
400,	207
500,	213

For glass (kind not specified), Dulong and Petit<sup>2</sup> found, for the coefficient of cubic expansion  $3\beta$ , from 0° to  $t^\circ$ , the mean value

$$0.0000251 + 10^{-11} 6t^2;$$

<sup>1</sup> *Com. Ren.*, 108, 1096 (1889); *Beiblätter*, 13, 644.

<sup>2</sup> Winkelm., *Handbuch*, II. 2, 48.



the experiments going up to 300°. This would give, for the cubical coefficient,

	Mean $\times 10^7$ .
0° to 100°,	257
200,	275
300,	305
400,	347
500,	401

These values of  $\alpha$  and  $\beta$  would give, at the temperature  $t^\circ$ , the values

$t$	$(2\alpha - 4\beta)t \times 10^5$
100°	+ 37
200°	+ 46
300°	- 14
400°	- 196
500°	- 545

This would make the correction vanish at some temperature between 200° and 300°; at lower temperatures it would be positive, and at higher negative.

From equation (2) we easily deduce

$$\frac{E'_t}{E'_{20}} = \frac{E_t}{E_{20}} [1 + (2\alpha - 4\beta)_t t - (2\alpha - 4\beta)_{20} 20].$$

This equation would serve for correcting the values given in the table of p. 164, if the coefficients of expansion of the different glasses were known. The correction has most interest in the case of those glasses which show the smallest diminution of elasticity with rise of temperature. Glass 34 is the most marked example, and a rough calculation for it has been made by Winkelmann in the following way:

From the chemical composition of the glass, its coefficient of linear expansion between 0° and 100° has been computed to be  $61 \times 10^{-7}$ . Adopting this value for  $\beta$  and  $186 \times 10^{-7}$  for  $\alpha$ , the value of  $2\alpha - 4\beta$  is  $128 \times 10^{-7}$ , which, multiplied by 20, gives  $256 \times 10^{-6}$ . We have, accordingly,

$$\frac{E'_t}{E'_{20}} = \frac{E_t}{E_{20}} [1 + (2\alpha - 4\beta)t - 256 \times 10^{-6}].$$

Hence the following corrected values are found :

GLASS No. 34.

$t$	$(1 - E_t/E_{20}) \cdot 100$	$(1 - E'/E'_{20}) \cdot 100$
100°	0·10	- 0·01
200°	0·23	- 0·04
300°	0·36	- 0·09
400°	0·49	- 0·16
500°	0·62	- 0·26

The minus signs indicate that the elasticity increases with rise of temperature, but the calculation assumes  $\beta$  to have the constant value  $61 \times 10^{-7}$ . If the mean value of  $\beta$  from 0° to 500° is greater than this by about 25 per cent., the elasticity at 500° will be about equal to that at 20°.

It therefore seems probable that for glass 34 the change of elasticity with temperature is scarcely sensible. The same remark applies to glass 19. For the other glasses, further knowledge of their expansions at high temperatures would be required before the correction could be made.

**75. Investigations on the Hardness of Glass**, and on properties associated with hardness, have been published by F. Auerbach.<sup>1</sup> His observations extend to 14 glasses, and to various other substances, ranging over the whole of Mohs' scale with the exception of diamond and talc. The chemical compositions of these glasses, except No. 11, are given in the following table :

<sup>1</sup> See the following papers :

- I. Absolute measurement of hardness. *Götting. Nachr.*, 6 Dec. 1890.
- II. Same title, *Ann. d. Phys. u. Chem.*, 43, 61 (1891).
- III. Hardness, brittleness, and plasticity. *Verhandl. d. Ges. deutsch. Naturf. u. Aerzte*. 1891.
- IV. On the measurement of hardness, especially in plastic bodies. *Ann. d. Phys. u. Chem.*, 45, 262 (1892).
- V. Plasticity and brittleness. *Idem*, 45, 277 (1892).
- VI. Hardness and elastic qualities of glass. *Id.*, 53, 1000 (1894).
- VII. Absolute scale of hardness. *Id.*, 58, 357 (1896).

Auerb.	W.	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	ZnO	PbO	Al <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>5</sub>	BaO	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	P <sub>2</sub> O <sub>5</sub>	Mn <sub>2</sub> O <sub>3</sub>
1	II	—	69.0	2.5	—	—	0.4	—	4.0	16.0	8.0	—	0.1
2	I	33	29.3	—	—	67.5	—	0.2	—	—	3.0	—	—
3	III	—	70.25	10.0	—	—	0.2	—	10.0	9.5	—	—	0.05
4	IV	20	20.0	—	—	80.0	—	—	—	—	—	—	—
5	—	5	71.0	14.0	—	—	5.0	—	10.0	—	—	—	—
6	—	25	70.6	—	12.0	—	—	0.4	—	17.0	—	—	—
7	—	23	34.5	10.1	7.8	—	5.0	0.5	42.0	—	—	—	0.1
8	—	2	—	69.1	—	—	18.0	0.2	4.7	8.0	—	—	—
9	—	21	32.7	31.0	—	25.0	7.0	0.3	—	1.0	3.0	—	—
10	—	26	41.0	—	—	51.7	—	0.2	—	—	7.0	—	0.1
11	—	—	—	—	—	—	—	—	—	—	—	—	—
12	—	6	67.3	2.0	7.0	—	2.5	—	14.0	—	7.0	—	0.1
13	—	10	58.7	—	—	—	—	0.3	—	—	33.0	8.0	—
14	—	13	—	3.0	—	—	8.0	1.5	28.0	—	—	59.5	—

The first column contains Auerbach's numbering of the glasses; the second his previous numbering of the first four; the third the corresponding numbers in Winkelmann's list (Art. 67). As regards Auerbach's 4 and 8, they were of the same composition as Winkelmann's 20 and 2, but were not from the same meltings. No. 11 is the so-called "Gerätéglass" (*flask or laboratory glass*). No. 12 is thermometer glass (Jenaer Normalglas).

The most important outcome of Auerbach's work is its experimental confirmation and completion of a theoretical investigation by H. Hertz<sup>1</sup> "on the contact of elastic solids." The following is a sketch of the results of this theory, so far as required for our purpose.

**76. Contact of a Plane Glass Plate with a Glass Lens under Pressure.** Hertz discusses the general case of two elastic isotropic bodies exerting mutual normal pressure over a small area common to both. An absence of tangential force is assumed. The investigations relate to the form of the surface of contact, the form and magnitude of its bounding curve, and the distribution of the pressure.

<sup>1</sup> *Journ. f. d. reine u. angewandte Mathematik*, 92, 156 (1882).

The results are very simple for two bodies of exactly the same material, if the surface of one previous to contact is plane and that of the other spherical; conditions which are practically fulfilled when a lens is pressed against a plate of the same glass. The surface of contact in this case is a portion of a sphere, its radius of curvature  $\rho'$  being double that of the given sphere, that is,

$$\rho' = 2\rho, \dots\dots\dots(1)$$

$\rho$  denoting the radius of curvature of the lens.

The boundary of the surface of contact is, of course, a circle. Let  $d$  denote its diameter,  $p$  the amount of the mutual pressure of the lens and plate,  $\mu$  the value of "Poisson's ratio" (see Art. 85) and  $E$  that of Young's modulus. Then  $d$  is determined by

$$d = \sqrt[3]{\frac{12p\rho(1-\mu^2)}{E}}, \dots\dots\dots(2)$$

and the intensity of pressure at the middle point is

$$p_1 = \frac{6p}{\pi d^2} \dots\dots\dots(3)$$

**77. Confirmation of the Theory, and Calculation of Indentation-Modulus.** In the apparatus designed by Auerbach and made by Zeiss,<sup>1</sup> a lens is pressed up by levers against a plate fixed in a horizontal position, and the surface of pressure is observed from above by means of a microscope with a micrometer eyepiece. The commencement of contact, before the pressure becomes sensible, is recognised by the first appearance of blackness in the centre of the interference rings. When pressure is applied, the surface of contact is seen as a round black spot—of size depending on the pressure. Simultaneous values of  $p$  and  $d$  can accordingly be observed.

Equation (2) can be written in the form

$$\frac{12p\rho}{d^3} = \frac{E}{1-\mu^2}, \dots\dots\dots(1)$$

which implies that  $p\rho/d^3$  is constant for a given material when  $\rho$ ,  $p$ , and  $d$  vary. This theoretical deduction obtained by Hertz

<sup>1</sup> The full description of the apparatus and observations is contained in papers I. and II.



is abundantly confirmed by Auerbach's experiments. The quotient  $p/d^3$  was found to be in general constant for the same  $\rho$  and to vary inversely as  $\rho$ .

The following is a specimen<sup>1</sup> of the results for glass 1, which is described as of medium hardness. The radius of curvature  $\rho$  of the lens was 10 mm.

$p$ .	$d$ .	$p/d^3$ .
2.2 kg.	0.33 mm.	62.1 kg/mm <sup>3</sup> .
3.5	.39	59.0
5.4	.45	60.3
7.4	.50	59.1
9.3	.54	59.1
13.3	.62	59.2
15.2	.63	59.9
16.4	.67	55.5
18.9	.69	56.8
31.1	.82	56.8
31.6	.82	56.9
36.5	.87	56.1
44.6	.91	58.9

The mean of the values of  $p/d^3$  is 58.4 kg. per square millimetre.

With varying values of  $\rho$  the following results were obtained for glass 1 :

$\rho$ .	$\frac{p}{d^3}$ .	$\frac{p\rho}{d^3}$ .
3 mm.	195.4 kg/mm <sup>3</sup> .	586 kg/mm <sup>2</sup> .
5	114.9	575
10	58.3	583
15	38.3	575

The numbers in the last column agree fairly well, and their mean 580 is accordingly to be regarded as a constant belonging to this kind of glass.<sup>2</sup>

Auerbach adopts  $\frac{E}{1-\mu^2}$  as the measure of *resistance to indent-*

<sup>1</sup> I. 532 and II. 86; all results being reduced to the kg. and mm.

<sup>2</sup> Auerbach, I. 533 and II. 88. A subsequent recalculation gave a somewhat larger value—see VI. 1003.

ation, and calls it the *indentation-modulus* (Eindringungsmodul). He denotes it by the symbol  $E'$ . We have, accordingly,

$$E' = \frac{E}{1 - \mu^2} \dots \dots \dots (2)$$

The values of this modulus for 14 glasses, as determined by Auerbach (VI. 1028), are given in the following table, together with the values of  $E$  and  $\mu$ . The values assigned to  $E$  are the

A.	W.	$E'$	$E$	$E' - E$	$\mu$
1	—	7107 kg/mm <sup>2</sup>	— kg/mm <sup>2</sup>	— %	—
2	33	5871	5494	6·4	0·25
3	—	7869	7461	5·2	0·23
4	20	5588	5088	8·9	0·30
5	5	7599	7296	4·0	0·20
6	25	6796	6632	2·4	0·16
7	23	8192	7972	2·7	0·16
8	2	4975	4802	3·5	0·19
9	21	5677	5471	3·6	0·19
10	26	5953	5464	8·2	0·29
11	—	7532	—	—	—
12	6	7792	7402	5·0	0·22
13	10	6197	6014	3·0	0·17
14	13	6811	6334	7·0	0·26

means of  $E_1$  and  $E_2$  (in the notation of Art. 72), except that, in the case of glass 5,  $E_1$  is adopted, because  $E_2$  was for a different melting. For glass 3, no determination of  $E$  was made; the value 7461 given in the table was obtained by Winkelmann for a glass of nearly but not exactly similar composition.

The differences between  $E'$  and  $E$  are given as percentages of  $E'$ , in the column headed  $E' - E$ .

**Calculation of Poisson's Ratio.** The numbers in the last column are the values of Poisson's ratio  $\mu$ , calculated from  $E'$  and  $E$  by means of equation (2).

The probable errors in the values of  $E'$  average  $\frac{1}{2}$  per cent., and never quite reach 1 per cent. Assuming the probable error of  $E$  to be  $\frac{1}{4}$  per cent., Auerbach deduces 7 per cent. as the probable limit of error for  $\mu$  (see Art. 85 for Straubel's determination).

These results establish the fact that  $\mu$ —the ratio of lateral contraction to longitudinal extension under longitudinal pull—is very different for different glasses. The view that it has the constant value  $\frac{1}{4}$  for all homogeneous isotropic bodies is therefore clearly untenable.<sup>1</sup>

**78. Law of Limiting Pressure.** If the pressure of the lens against the plate, as described in the foregoing article, is gradually and slowly increased to a sufficient degree, the plate suddenly cracks; the crack being of circular form and concentric with the area of contact. Its diameter exceeds that of the circle of contact by—on the average—about 19 per cent., for glasses of all kinds.

We shall denote by  $P$  the value of the total pressure  $p$  at which this result occurs; we may call it the *limiting amount of pressure*. Auerbach determined its value for the glasses 1-14, and arrived at the simple law that, for a given material, *the limiting amount of pressure  $P$  is proportional to the radius of curvature  $\rho$* , so that

$$\frac{P}{\rho} = F',$$

$F'$  being a constant depending only on the material. This constant, which measures the resistance of the material to fracture by indentation, has not yet received a name. It may be provisionally called the *fracture-modulus*. The degree of accuracy with which this law is fulfilled in the case of glass 1 is shown in the following table:

$\rho$ .	$P/\rho$ .
3 mm.	4.93 kg/mm.
5	4.78
10	5.04
15	4.80

The mean is  $F' = 4.89$  kg/mm.

**79. Absolute Measurement of Hardness.** Auerbach undertook his investigations<sup>2</sup> for the express purpose of obtaining

<sup>1</sup> See Art. 85.

<sup>2</sup> A review of previous measurements of hardness is given in Auerbach, II. 64.

absolute measurements of hardness. His method of experiment does not involve the properties of any material other than that whose hardness is in question.

The direct data given by his experiments are: the indentation-modulus  $E'$ , and the fracture-modulus  $F'$ . The question arises: in what relation do these two constants stand to the property expressed by the name "hardness"? The first experiment, made on the glasses 1, 2, 3, and rock crystal, sufficed to show that  $F'$  was not identical with hardness; for glass 2, described by the makers as "soft," has a decidedly larger value of  $F'$  than 1 and 3, of which the former was described as "of medium hardness," and the latter as "tolerably hard."<sup>1</sup>

If a less hard body is able, with equal  $\rho$ , to bear a greater amount of pressure  $P$ , the explanation which first suggests itself is that it spreads the pressure over a wider surface, and that the limiting value  $P_1$  of the *intensity* of pressure  $p_1$  is the essential consideration. In fact, for equal  $\rho$ , the soft glass 2 bore the smallest  $P_1$ , and the hard glass 3 the greatest.

Hertz assumed *a priori* that the limiting intensity  $P_1$  at the centre of the pressure-area, when the limit of elasticity is reached, is a constant for the material, independent of  $\rho$ ; and he accordingly adopted this limiting value  $P_1$  as the measure of the hardness of the material.<sup>2</sup> The passing of the limit of elasticity is easily recognised, in brittle bodies, by the formation of a crack, as in Auerbach's experiments. In plastic bodies it would be necessary to determine the pressure at which permanent deformation begins.

If Hertz's assumption were correct,  $P_1$  would be a definite function of  $E'$  and  $F'$ . Introducing, in equations (2) and (3) of Art. 76, the limiting values  $P$ ,  $P_1$ ,  $D$  of  $p$ ,  $p_1$ ,  $d$ , and employing the law of limiting pressure, we obtain the three equations:

$$D = \sqrt[3]{\frac{12P\rho}{E'}},$$

$$P_1 = \frac{6P}{\pi D^2},$$

$$\frac{P}{\rho} = F';$$

<sup>1</sup> Compare Auerbach's concluding remarks, I. 541 and II. 100.

<sup>2</sup> *Verh. d. Berl. phys. Ges.* 1882, 67; *Verh. d. Ver. z. Förder. d. Gewerbflusses*, 1882, 441; *Gesamm. Werke*, I, 174.



from which the three following are deducible :

$$P_1 \sqrt{D} = \frac{1}{\pi} \sqrt{3E'F'}, \dots\dots\dots(1)$$

$$P_1 \sqrt[3]{P} = \frac{1}{\pi} \sqrt[3]{\frac{3}{2}E'^2F'^2}, \dots\dots\dots(2)$$

$$P_1 \sqrt[3]{\rho} = \frac{1}{\pi} \sqrt[3]{\frac{3}{2}E'^2F'}. \dots\dots\dots(3)$$

$P_1$  is therefore not a definite function of  $E'$  and  $F'$ , and is not the sole determining element of hardness.

The problem of obtaining, by further development of Hertz's theory, a useful definition of hardness is as yet unsolved.

Proceeding empirically, and accepting  $P_1$  as one determining element of hardness, equations (1), (2), (3) offer a choice between

$$P_1 \sqrt{D}, \quad P_1 \sqrt[3]{P}, \quad P_1 \sqrt[3]{\rho},$$

as measures of hardness. Applying these to the three glasses 1, 2, 3, and observing that they depend respectively on  $E'F'$ ,  $(E'F')^2$ , and  $E'^2F'$ , we find that the hardest glass 3 has the largest  $E'F'$ , but the glass of intermediate hardness 1 has the smallest. On the other hand, the largest value of  $E'^2F'$  belongs to the hardest glass 3, and the smallest value to the softest glass 2.

It would therefore appear that the hardness  $H$  is best defined by the equation

$$H = P_1 \sqrt[3]{\rho}, \dots\dots\dots(4)$$

and can be experimentally determined by the help of the equation

$$H = \frac{1}{\pi} \sqrt[3]{\frac{3}{2}E'^2F'}. \dots\dots\dots(5)$$

The following table contains (in the last column) the values of  $H$  deduced by Auerbach from his observations.<sup>1</sup> The glasses are here arranged in ascending order of hardness, and the values of

<sup>1</sup> Auerbach, VI. 1014.

$E'$  and  $F'$  from which  $H$  is derived are also given.<sup>1</sup> The radii of curvature  $\rho$  of the lenses employed are also given.

No.	$\rho$ in mm.	$E'$ in $\frac{\text{kg}}{\text{mm}^2}$	$F'$ in $\frac{\text{kg}}{\text{mm}}$	$H$ in $\frac{\text{kg}}{\text{mm}^{5/3}}$
10	2, 5, 7	5953	3.0	173
4	1, 2, 4	5588	4.1	183
2	1, 4, 12	5871	5.6	210
14	2, 5	6811	4.6	217
8	1, 3, 5	4975	8.8	219
1	3, 5, 10, 15	7107	4.5	223
9	3, 5	5677	9.3	244
3	4, 12, 30	7869	5.0	246
12	2, 5	7792	6.4	266
11	2, 5	7532	6.9	267
6	1, 3, 9	6796	9.0	272
5	1, 5	7599	7.4	274
13	2, 5	6197	11.6	278
7	1, 3, 5	8192	9.7	316

In connection with the definitions of hardness, it may be of interest to state that the arrangement of the glasses in ascending order of the product  $E'F'$  is: 10, 4, 14, 1, 2, 3, 8, 12, 11, 9, 5, 6, 13, 7.

The ratio of 173 to 316 is 1 to 1.83. The greatest hardness is accordingly not so much as double of the least.

**80. Experiments on Scratching.** The comparative hardness of different bodies has hitherto been decided almost exclusively by the test of scratching. It was therefore important to ascertain how far this test agreed with the foregoing determinations. Auerbach accordingly carried out a series of experiments on the 14 glasses in question in the following manner.<sup>2</sup>

Broken pieces of all the 14 glasses were provided, each having at least one point which appeared to be neither too blunt nor too fragile. The mode of experimenting was to make one of these points rest upon the plane surface of another kind of glass at an

<sup>1</sup> Auerbach does not state the values of  $F'$ ; they are deducible from  $H$  and  $E'$  by equation (5).

<sup>2</sup> Auerbach, VI. 1015.

inclination of about  $60^\circ$ , and then to move it under strong pressure. This was done with every glass upon every other, the whole number of combinations being  $14 \times 13 = 182$ .

It turned out that every glass was scratched by every other, even the hardest by the softest. In order to decide between two glasses, it was therefore necessary to find which of them exhibited the greater scratching power upon the other. With this view the scratches were examined under the microscope. This showed not only quantitative but qualitative distinctions. There were scratches with lateral chipping, with lateral cracking, with lateral splintering, with longitudinal cracking, with longitudinal splintering, with cavities leaf-shaped or shell-shaped or irregular.

When no decided superiority in scratching-power was detected in the comparison of two glasses, they were adjudged to be equally hard.

Out of the whole 91 comparisons of the glasses, two and two, (this being the number of combinations of 14 things, two together), there were 18 departures from the order of relative hardness found above. They are exhibited in the following list, in which the numbers are those of the list in Art. 79.

$$10 > 4; \quad 2 = 8; \quad 1 > 9; \quad 1 = 11;$$

$$9 = 13; \quad 3 = 11; \quad 3 > 6; \quad 3 = 5;$$

$$12 > 11; \quad 12 > 6; \quad 12 = 13;$$

$$11 > 6; \quad 11 = 5; \quad 11 > 13; \quad 11 > 7;$$

$$6 = 5; \quad 5 > 13; \quad 5 > 7.$$

The largest discrepancy is  $11 > 7$ ; for 7 is 49 units harder than 11 according to the values of  $H$  in Art. 79.

If we attempt to arrange these glasses in the order of their scratching powers, 4 is the softest, and 10 comes next. But there are inconsistencies which render a continuous arrangement impossible. Thus we have

$$2 < 14 < 8, \text{ with } 2 = 8,$$

$$9 < 1 < 13, \text{ with } 9 = 13,$$

$$11 = 5; \quad 6 = 5, \text{ with } 11 > 6;$$

and still worse,

$$7 < 11 < 12, \text{ with } 7 > 12.$$

**Active and Passive Scratching Hardness.** With the help of microscopic examination, Auerbach distinguished 10 degrees of strength in the scratches. Numbering these from 1 to 10, 1 being the weakest and 10 the strongest, he obtained a numerical value for the scratching power of each glass by adding the values of the scratches made by it upon the other 13. In like manner he obtained a numerical value for susceptibility to scratching by adding the values of the scratches made upon any one glass by the other 13. The results are shown in the following table, in which the top row contains the numbers of the glasses when arranged in order of their values of  $H$ , beginning with the softest; the second row contains their scratching powers, and the third row their susceptibility to scratching:

10	4	2	14	8	1	9	3	12	11	6	5	13	7
17	31	36	41	45	55	53	68	64	78	63	75	66	68
82	100	79	71	60	46	51	33	32	46	45	42	48	27

There is no regular law of connection either between the first row and the other two, or between the last two rows themselves.

**81. The Absolute Hardness of Glass and its Chemical Composition.** Auerbach made the attempt to express the "absolute hardness" of glass in terms of the percentages of its constituent oxides, in the same way in which other properties have been expressed (for example in Art. 69).

Neglecting the small percentages of  $\text{As}_2\text{O}_5$  and  $\text{Mn}_2\text{O}_3$  contained in some of the glasses, he assigned to the 10 remaining oxides the following coefficients:

$\text{SiO}_2 = 3.32$	$\text{BaO} = 1.95$
$\text{B}_2\text{O}_3 = 0.75$	$\text{Na}_2\text{O} = -2.65$
$\text{ZnO} = 7.1$	$\text{K}_2\text{O} = 3.9$
$\text{PbO} = 1.45$	$\text{CaO} = -6.3$
$\text{Al}_2\text{O}_3 = 10.2$	$\text{P}_2\text{O}_5 = 1.32$

Multiplying the percentages given in Art. 75 by these coefficients, we obtain the values headed "Calculated" in the following table. The differences between these and the "Observed" values are so



large, especially in the case of the lead silicate glass 10, that the representation fails.

	Absolute Hardness in $\text{kgmm}^{-5/8}$		
	Observed.	Calculated.	Obs.-Calc.
1	223	232	- 4 %
2	210	207	+ 1
3	246	251	- 2
4	183	182	+ 1
5	274	270	+ 1
6	272	275	- 1
7	316	310	+ 2
8	219	222	- 1
9	244	248	- 2
10	173	238	-38
11	267	—	—
12	266	219	+18
13	278	273	+ 2
14	217	216	+ 0

**82. Unequal Brittleness of different Glasses.** If the experimental method described in Art. 77 is applied to plastic bodies, for example, to rock salt or fluorspar, the result of overstepping the elastic limit is not a crack, but a permanent deformation—a depression in the plate and a flattening of the lenses. These permanent effects increase gradually with increasing pressure; and it is impossible to determine the exact pressure which corresponds to the elastic limit. The limiting intensity of pressure is therefore not a suitable criterion for the determination of hardness in such bodies.

When the increase of pressure is carried beyond the elastic limit, equation (2) of Art. 76 no longer holds; thus Auerbach found, for rock salt and fluorspar, that in a series of experiments with given  $\rho$  the quotient  $p/d^3$  did not remain constant, but rapidly decreased as the pressure increased beyond a certain amount. If, however, the *intensity* of pressure in the centre of the pressure-area is calculated by equation (3), this is found to reach a maximum  $P_1$  which remains constant as the pressure is further increased. In this case, then, we have

$$P_1 = \frac{6}{\pi} \lim \left( \frac{p}{d^2} \right).$$

The following values were found for fluorspar:<sup>1</sup>

$\rho$	$P_1$
3 mm	73.7 kg/mm <sup>2</sup>
5	61.4
10	49.1

For brittle as well as for plastic bodies,  $P_1$  can accordingly be defined as the limiting pressure-intensity in the centre of the pressure-area.

This limiting value follows the same laws in the case of plastic as of brittle bodies, and the product  $P_1\sqrt[3]{\rho}$  is constant. Thus the above values give

$\rho$	$P_1\sqrt[3]{\rho}$
3 mm	106 kg mm <sup>-5/3</sup>
5	105
10	106

Auerbach accordingly defines the hardness  $H$  of plastic bodies (as well as of brittle bodies) by the equation

$$H = P_1\sqrt[3]{\rho}; \dots\dots\dots(1)$$

and derives it from observations by the equation<sup>2</sup>

$$H = \frac{6}{\pi}\sqrt[3]{\rho} \cdot \lim \left( \frac{p}{d^2} \right) \dots\dots\dots(2)$$

It is worthy of mention that the quantitative laws found by Auerbach for plastic minerals have been confirmed by observations made by A. Föppl on a series of metals. The specimens had one side ground to a cylindrical form, and two of these cylindrical faces, laid across each other at right angles, were pressed together. In order to permit of subsequent measurement of the area of contact, one of the cylindrical surfaces was covered with a fine layer of soot. The pressure-area was found to vary

<sup>1</sup> Auerbach, IV. 268.

<sup>2</sup> Equation (2) of course holds also for brittle bodies. For these we have

$$\lim \left( \frac{p}{d^2} \right) = \frac{P}{D^2},$$

but the limiting value  $D$  cannot be directly observed with certainty. On the other hand, for plastic bodies the indentation-modulus can only be determined by observations within the elastic limit.

directly as the total pressure; the average intensity remained therefore unchanged, that is, it attained its limiting magnitude at an early stage. The product of this intensity and the cube root of the radius of the cylinder was found to be constant for a given metal.<sup>1</sup>

Plasticity and brittleness may be regarded as two extreme conditions between which there is a continuous transition; and calcspar seems to occupy an intermediate position.<sup>2</sup>

These properties may serve to throw light on some peculiar effects exhibited by certain kinds of glass.

Glasses 1, 8, 9, 12, 13, 14 gave constant values of  $p/d^3$  in all series of experiments; and so did glasses 6, 7, 11, except that in one series this quotient diminished with increasing pressure.

On the other hand, glasses 2, 4, 10 exhibited numerous and sometimes quite large departures from this rule. Take, for instance, the following data given<sup>3</sup> by Auerbach for glass 2, and obtained with a lens of radius of curvature  $\rho = 1$  mm.:

$p$	$\frac{p}{d^3}$	$\frac{6}{\pi} \sqrt[3]{\rho} \cdot \frac{p}{d^2}$
3.43 kg	488 kg mm <sup>-2</sup>	179 kg mm <sup>-5/2</sup>
4.41	475	191
5.39	426	190
7.35	405	203
9.31	417	224
11.27	365	219
17.15	299	220
19.11	283	220

As the pressure increases, the quotient  $p/d^3$  shows large diminution. At the same time the total pressure increases far beyond the normal limit  $P = 5.6$  kg., so that the law of limiting pressure is not fulfilled. These anomalies become intelligible, if we assume that the glass in question is less brittle than those which exhibit normal behaviour. This view is borne out by the numbers in the last column. These are the values of the quantity whose limit, as the pressure increases, is equal, by

<sup>1</sup> *Ann. d. Phys. u. Chem.*, 50, 101 (1897).

<sup>2</sup> Compare Auerbach, III. and V.

<sup>3</sup> The actual numbers given in Auerbach, VI. 1032, are here reduced to the kg. and mm.

equation (2), to the hardness  $H$ , in the case of a plastic body. This limit 220 is 5 per cent. greater than the value of  $H$  for glass 2 in the table of Art. 79.

Specially noteworthy appearances were exhibited by glass 4, a lead-silicate containing 80 per cent. of lead oxide, and distinguished by its deep yellow colour. The crack did not, in most cases, occur suddenly in this glass, but was formed gradually in the same manner as in calcspar; appearing first as a short line, which, as the pressure was increased, extended further, and finally formed a closed curve. In some cases it was not a decided crack that was seen, but what might rather be called fine furrows; and in these cases the series of observations did not follow the ordinary law, but resembled those above described for glass 2. The overstepping of the ordinary limit of pressure was the more easily obtained the more gradually the pressure was increased. The crack which at last occurred was then abnormally large, accompanied, however, by a concentric crack of normal size. In some cases it was found possible by means of a blow to produce three concentric cracks, the smallest of the three being of the normal size.<sup>1</sup> These appearances may also be regarded as indications of imperfect brittleness.

### 83. Position of Glass in the General Scale of Hardness.

Auerbach has extended his method of determination of absolute hardness to the minerals of Mohs' scale of hardness, with the exception of its two extreme members, talc and diamond.<sup>2</sup> The results are collected in the following table, and as the materials are not isotropic, the direction of the pressure in the plate and lens is stated in each case.

Direction.		Hardness.
Gypsum, - -	Perpendicular to cleavage, - -	14 kg mm <sup>-5/3</sup> .
Rock salt, - -	„ face of cube, - -	20
Calcspar, - -	„ cleavage, - -	92
Fluorspar, - -	„ octahedral face, - -	110
Apatite, - -	Along axis, - - - -	237
Felspar (adular),	Perpendicular to base, - - -	253
Quartz, - -	Along axis, - - - -	308
Topaz, - -	Perpendicular to base, - - -	525
Corundum, -	Along axis, - - - -	1150

<sup>1</sup> Auerbach, IV. 272; V. 290.

<sup>2</sup> Auerbach, VII.



Of these minerals, corundum, topaz, quartz, and felspar are brittle; gypsum, rock salt, and fluorspar plastic; calcspar and apatite imperfectly brittle.

According to these numbers, the borosilicate crown glass 7 is harder than quartz, and even the soft lead flint glasses are considerably harder than fluorspar. Auerbach has suggested filling the large gaps in the middle part of Mohs' scale by inserting the crown of hardness 274 between quartz and felspar, and two flints of hardness 210 and 170 between apatite and fluorspar.

In his attempt (Art. 81) to give a formula for calculating the hardness of glass from its chemical composition, Auerbach assigned the coefficient 3.32 to  $\text{SiO}_2$  and 10.1 to  $\text{Al}_2\text{O}_3$ . He calls attention to the agreement of these numbers when multiplied by 100 with the hardness of quartz and corundum as given in the above list,<sup>1</sup> especially in view of the fact that the maximum hardness of corundum is for pressure in the direction of the axis, its mean hardness being somewhere about 100 units less.

**84. Relations between Hardness and other Properties of Glass.** Comparisons of the hardness of glass with its tenacity, its resistance to crushing, and its modulus of elasticity have not led to any distinct conclusions.<sup>2</sup> Auerbach remarks that for the most part hardness increases with resistance to crushing and with Young's modulus. The mean value of resistance to crushing is 74 for the five soft glasses 10, 4, 2, 14, 8, and is 95 for the five hard glasses 9, 6, 5, 13, 7. The mean value of Young's modulus is 6051 for the six soft glasses 10, 4, 2, 14, 8, 1, and is 7196 for the eight hard glasses 9, 3, 12, 11, 6, 5, 13, 7.

Auerbach suspects a close relation between hardness and Poisson's ratio. He gives the following list of the values of the hardness  $H$ , the Poisson ratio  $\mu$ , and their product  $\mu H$ :

No.	$H$ .	$\mu$ .	$\mu H$ .
10	173	.29	50
4	183	.30	55
2	210	.25	35
14	217	.27	57
8	219	.24	53
9	244	.19	46

<sup>1</sup> Auerbach, VII. 364 and 369.

<sup>2</sup> Auerbach, VI. 1022, 1031.

No.	$H$ .	$\mu$ .	$\mu H$ .
3	246	·23	57
12	266	·21	54
6	272	·21	57
5	274	·20	55
13	278	·17	48
7	316	·17	54

The last column shows that the product of  $\mu$  and  $H$  for glass is approximately constant.<sup>1</sup>

Hertz has calculated,<sup>2</sup> for the general case of two spheres pressed together, the diminution of distance between their undistorted portions. For the case of a lens pressed against a plate, the general formula reduces to

$$g = \frac{3}{E'} \cdot \frac{p}{d}, \dots\dots\dots (1)$$

$g$  denoting the amount of approach in question.<sup>3</sup> Eliminating the diameter  $d$  by equation (2) of Art. 76, we have

$$g = \sqrt[3]{\left(\frac{3}{2} \frac{p}{E'}\right)^2 \frac{1}{\rho}} \dots\dots\dots (2)$$

To compute the maximum value  $G$  of  $g$  (which is attained immediately before cracking), we must give  $p$  the value  $P$ , and by employing the equation  $P/\rho = F'$  of Art. 78, we obtain

$$G = \sqrt[3]{\left(\frac{3}{2} \frac{F'}{E'}\right)^2 \rho} \dots\dots\dots (3)$$

Instead of the modulus of limiting pressure  $F'$ , we may introduce the hardness  $H$ , by means of equation (5), Art. 79. This gives

$$G = \left(\pi \frac{H}{E'}\right)^2 \rho^{\frac{1}{3}} \dots\dots\dots (4)$$

The depth of the depression in the glass plate, at any time during the application of the pressure, can be shown to be almost exactly  $\frac{1}{2}g$ , or, at the instant of cracking,  $\frac{1}{2}G$ .

<sup>1</sup>[This conclusion is overturned in the last article of this chapter.]

<sup>2</sup>*Jour. f. d. reine u. angew. Math.*, 92, 166.

<sup>3</sup>From equation (1) it is easy to deduce  $g = \frac{1}{4} \frac{d^2}{\rho}$ , which is a convenient formula for the direct calculation of  $g$  from observations.

$G$  is the greatest amount of linear compression of the system composed of lens and plate, before cracking. It varies as the cube root of the radius of curvature  $\rho$  of the lens; and the quotient

$$G/\rho^{\frac{1}{3}} = \left( \pi \frac{H}{E'} \right)^2 \dots \dots \dots (5)$$

is a constant of the material. It may be called "the limit of linear compressibility of a brittle substance in experiments on absolute hardness." Its values for the 14 glasses are given in the following list:

No.	$H$	$G/\rho^{\frac{1}{3}}$
10	173	0.0083 mm <sup>2/3</sup>
4	183	.0106
2	210	126
14	217	100
8	219	191
1	223	97
9	244	182
3	246	96
12	266	115
11	267	124
6	272	158
5	274	128
13	278	199
7	316	147

The second column contains the hardness in ascending order. Comparison of the two columns shows that for the most part (with some marked exceptions) increase of hardness gives increase of limiting compressibility. The mean value for the first six glasses is .0117, and for the last eight glasses .0144.

**85. Poisson's Ratio.** [The name *elasticity number* (Elasticitätszahl) is given in Germany to the ratio denoted by  $\mu$  in the foregoing articles. In England it is usually called *Poisson's ratio*, because Poisson maintained that it had the constant value  $\frac{1}{2}$  for all isotropic bodies. It is usually defined as "the ratio of lateral contraction to longitudinal extension (or of lateral bulging to

longitudinal compression) when a cylindrical portion of the substance is subjected to longitudinal pull (or thrust)." More precisely, let  $L$  and  $D$  be the length and diameter of the cylinder before, and  $L+l$ ,  $D+d$  after, the application of the pull or thrust; then the ratio in question is

$$-\frac{d}{D} \frac{L}{l} = \mu.$$

The value of this ratio for the different kinds of glass has recently been investigated by R. Straubel.<sup>1</sup> He begins with a brief account of the previous investigations of Everett, Cornu, Voigt, Cantone, Kowalski, and Amagat, and gives the preference to Cornu's method.

Cornu employed glass plates or strips, of rectangular section, and of various thicknesses, supported horizontally on two parallel knife-edges; and subjected them to flexure by hanging on weights at their ends. The upper surface of the glass thus acquires a peculiar deformation, which can be observed by means of interference fringes, and made the basis of calculation for Poisson's ratio. Straubel produces the same deformation in nearly the same way, but employs a different method of observing the interference fringes—a method indicated (though not employed) by Cornu.

When the longitudinal axis of the strip is bent into an arc convex upwards, the transverse axis is at the same time bent into an arc convex downwards. The surface of the strip, originally plane, acquires anticlastic curvature (or becomes saddle shaped), and the curvature in the transverse section is  $\mu$  times the curvature in the longitudinal section.<sup>2</sup>

If the lower (plane) face of a circular cover-plate, parallel to the tangent plane at the centre of the upper surface of the strip, is brought into close proximity with this surface, and illuminated by normally incident monochromatic light, an interference pattern, consisting of two conjugate systems of hyperbolas, will be produced, as represented in fig. 20. Let  $\alpha$  be the angle at which each asymptote is inclined to the transverse section;<sup>3</sup> then  $\tan^2 \alpha$

<sup>1</sup> *Ann. d. Phys. u. Chem.*, 68, 369 (1899).

<sup>2</sup> Thomson and Tait, II. 250; also Winkelmann, *Handb. d. Phys.*, I. 263.

<sup>3</sup> [In the figure, the transverse section is nearly vertical.]



is the ratio<sup>1</sup> of the transverse to the longitudinal curvature (neglecting sign), and we have

$$\mu = \tan^2 \alpha.$$

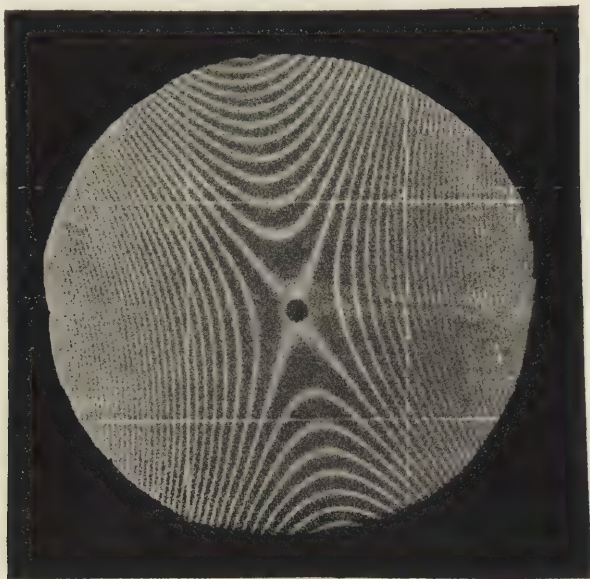


FIG. 20.

The glass strip, resting on a pair of knife-edges, was pressed up against a second pair of knife-edges, further apart, and symmetrically placed.<sup>2</sup> As a rule, the distance between the first pair was 7 cm., and between the second pair 10 cm. To prevent undesirable reflections, the cover-plate was slightly wedge-shaped, the angle of the wedge being 20', and the under side of the glass strip was roughened. The under side of the cover-plate was etched with cross rulings.

The source of light employed was a hydrogen vacuum tube worked by a coil. For eye observation, a red glass (coloured

<sup>1</sup>Knoblauch, *Theor. d. krummen Flächen* (1888) p. 126. Hoppe, *Principien d. Flächentheorie* (1890) p. 40.

<sup>2</sup>[This mode of producing flexure has the advantage, over that described in Art. 72, of giving a uniform bending torque in the portion of the strip between the inner knife-edges.]

with oxide of copper) served to suppress all the light except that belonging to the red hydrogen-line *C*. For photographing the pattern, the light was decomposed by two flint glass prisms, and the *F* component alone employed. In both cases, the light, after being made parallel, fell perpendicularly on the surfaces to be examined, and, on its return after reflection, entered either the camera or the observing telescope, passing on its way through an arrangement for measuring the wedge-angle  $\alpha$ .

In the subsequent measurement of angles on the photographic plate, a graduated revolving table was employed, belonging to a mineralogical microscope. The plate was laid on this table and centred, and the table was then turned till the two asymptotes in the pattern had been successively brought into parallelism with a fixed thread in the ocular. For measuring the details of the pattern, Pulfrich's apparatus<sup>1</sup> for interference measurements was found suitable, after its Dove prism had been fitted with a divided circle and vernier. Here again, by revolving the Dove prism, the directions of the asymptotes were made parallel to a fixed thread in the ocular, the angle between them being given by the difference of readings.

It was necessary to contend with the difficulty, or impossibility, of obtaining strips of so small a thickness as 2.5 mm. with sufficiently plane surfaces. In consequence of this defect, the strips almost always showed either a regular increase or a regular decrease of the angle  $\alpha$ , as the flexure was increased. Straubel therefore made, with each strip, a series of observations, with different amounts of flexure; and, from comparison of their differences, deduced the value of  $\alpha$  which would have been observed, if the surface of the strip had been originally plane. The calculation<sup>2</sup> was made by the method of least squares; account being taken of the fact that, as the flexure becomes greater, the observations become more trustworthy.

A complete testing of the method would involve a determination of the influence of the width and thickness of the glass plate, and of the distances between the knife-edges. Such tests were only partially made. The most important influence detected was that of the width of the plate. As the width increases,

<sup>1</sup> *Zeitschr. f. Instrumentk.*, 18, 261 (1898).

<sup>2</sup> Straubel, *l.c.* p. 385-390.

the theoretical assumptions on which the method rests are less strictly fulfilled, and the form of the surface is modified. By inserting thin slips of indiarubber between the glass and the knife-edges, the cross-bending was facilitated; and experiments, with glass plates 3 cm. wide and 3 mm. thick, showed the reality of the above-indicated sources of error, by a notable diminution in the value obtained for  $\mu$ .

For one particular glass the tests were very complete, and are fully described. Its trade number was 1991, and its composition

SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	ZnO	As <sub>2</sub> O <sub>5</sub>	BaO	Na <sub>2</sub> O	K <sub>2</sub> O	Mn <sub>2</sub> O <sub>3</sub>
65·22	2·7	1·5	0·5	10	5	15	0·08%

All the specimens of this glass were cut from a single plate, which was free from veins, stresses, and bubbles. Their widths were 1·0, 1·75, 2·0, 2·5, 3·0 cm., and their thicknesses 2·0, 2·5, 3·0 mm.

The distance between the inner knife-edges was sometimes 3·4 and sometimes 5·7 cm.; the distance between the outer ones was always 10 cm. The values found for  $\mu$  ranged from ·215 to ·233.

On the whole, Straubel concludes that he has obtained sufficiently constant determinations for the several kinds of glass which he examined. The question whether the constant values thus obtained are correct, can only be answered after comparison with results obtained by various methods, and must for the present be left open; though the answer is likely to be in the affirmative. If they are not correct as absolute values, they may be accepted as relative values, from which the absolute values can be inferred as soon as a few certain determinations are available.

Straubel has taken no account of the temperatures at which his observations were made. He states however that, judging from observations by Kowalski, the corrections for differences of temperature in different determinations may amount to ·003.

**List of the Glasses.** Straubel has given results for 29 different Jena glasses, and also for pure boric acid. Out of the 29, there are 20 which are included in Winkelmann's list (Art. 67), with the following differences in numbering:

W.	Str.	W.	Str.	W.	Str.
19	1450	27	S. 219	39	665
20	S. 208	28	2158	85	1973
21	658	30	290	86	2154
22	S. 196	31	270	87	627
23	1299	32	370	90	20
25	709	33	500	91	714
26	1571	38	16 <sup>III</sup>		

The widths of the plates or strips lay between 2 and 2.53 cm., and their thicknesses between 2.42 and 2.58 mm. The inner knife-edges were 7 cm. and the outer 10 cm. apart. These data apply to all the glasses except S. 95 and 665. For these, and for boric acid, the data were

	Breadth.	Thickness.
S. 95	1.40 cm.	2.36 mm.
665	1.65	1.56
Boric acid	1.78	3.34

For all three, the inner knife-edges were 5 and the outer 7 cm. apart. With the boric acid the regular series of observations was only partially carried out.

Eight of the nine glasses not included in Winkelmann's list had the following chemical compositions. For the remaining glass 278<sup>III</sup> the composition is not given.

No.	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	ZnO	PbO	Al <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>5</sub>	BaO	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	P <sub>2</sub> O <sub>5</sub>	Mn <sub>2</sub> O <sub>3</sub>
2175	68.7	8	—	—	—	1.5	—	5.3	14.5	2	—	0.03
1893	53.5	20	—	—	—	—	—	—	6.5	—	—	—
2106	44.6	—	—	46.6	—	0.3	—	0.5	8	—	—	—
2122	37.5	15	—	—	5	1.5	41	—	—	—	—	—
1933	39.64	6	9.2	—	2.5	0.5	42.1	—	—	—	—	0.06
S. 95	—	3	—	—	1.5	1.5	38	—	—	—	56	—
S. 185	—	71.8	—	—	22.4	—	—	—	—	—	—	—
S. 120	—	42.8	—	52	5	0.2	—	—	—	—	—	—

No. 1893 contained also 20 per cent. of Sb<sub>2</sub>O<sub>3</sub>.

S. 185 contained also 5.8 per cent. of Li<sub>2</sub>O.



Straubel endeavoured to express the value of  $\mu$  as a linear function of the percentages of the constituent oxides, and made out five different sets of coefficients, of which we shall only reproduce one. To calculate  $\mu$ , the percentages are to be multiplied by these coefficients, and the sum divided by 100.

SiO <sub>2</sub> ,	·1533	K <sub>2</sub> O,	·3969
B <sub>2</sub> O <sub>3</sub> ,	·2840	CaO,	·4163
ZnO,	·3460	P <sub>2</sub> O <sub>5</sub> ,	·2147
PbO,	·2760	Sb <sub>2</sub> O <sub>3</sub> ,	·2772
Al <sub>2</sub> O <sub>3</sub> ,	·1750	MgO,	·2500
BaO,	·3560	As <sub>2</sub> O <sub>5</sub> ,	·2500
Na <sub>2</sub> O,	·4310	Mn <sub>2</sub> O <sub>3</sub> ,	·2500

In the following table  $\mu$  denotes the observed and  $\mu'$  the calculated value. The difference  $\mu - \mu'$ , as compared with  $\mu$ , amounts on the average to 1·7 per cent., and in the worst case to 5 per cent. No coefficient is assigned to Li<sub>2</sub>O, and the single glass S. 185 which contains it is omitted from the calculation.

No.	$\mu$	$\mu - \mu'$	No.	$\mu$	$\mu - \mu'$
1450	·197	- ·003	658	·250	+ ·014
278 <sup>III</sup>	·208	+ ·001	1973	·252	- ·006
2175	·210	- ·010	290	·253	- ·002
627	·213	- ·008	270	·253	0
1893	·219	- ·001	2122	·256	- ·003
714	·221	+ ·002	370	·261	+ ·006
20	·221	+ ·003	S. 208	·261	+ ·010
2154	·222	- ·002	1933	·266	0
2106	·222	- ·009	1299	·271	+ ·003
1571	·224	- ·011	S. 95	·272	+ ·002
709	·226	+ ·002	S. 185	·273	—
16 <sup>III</sup>	·228	0	S. 196	·274	- ·005
2158	·231	- ·002	S. 120	·279	+ ·004
S. 219	·235	- ·002	B <sub>2</sub> O <sub>3</sub>	·283	- ·001
500	·239	- ·005	665	·319	- ·001

**Comparison with Auerbach.** The indirect determinations of the same element made by Auerbach (Art. 77) in connection with his experiments on hardness, when compared with Straubel's determinations for the same glasses, exhibit large discrepancies, as shown by the following table. Auerbach's estimate of 7 per

cent. as a probable limit of error, and 14 per cent. as the greatest possible error, in his values of  $\mu$ , seems to be much too favourable.

No.	Straub.	Auerb.	Diff.	No.	Straub.	Auerb.	Diff.
1450	0.197	0.20	- 1.5 %	290	0.253	0.17	+ 32.8 %
1571	0.224	0.29	- 29.5	270	0.253	0.27	- 6.7
709	0.226	0.21	+ 7.1	S. 208	0.261	0.30	- 14.9
16 <sup>III</sup>	0.228	0.21	+ 7.9	1299	0.271	0.17	+ 37.3
500	0.239	0.25	- 4.6	S. 196	0.274	0.24	+ 12.4
658	0.250	0.19	+ 24.0				

If we multiply Auerbach's values of the hardness  $H$  by Straubel's values of  $\mu$ , the products, instead of being nearly constant as in Art. 84, range from 38.8 to 120.3. The supposed connection between hardness and Poisson's ratio thus falls to the ground.

**Resistances to Compression and Shearing.** Let  $C$  denote the "volume-elasticity" or "resistance to compression," and  $T$  the "simple rigidity" or "resistance to shearing"—usually measured by experiments on the torsion of cylinders. Then, writing  $E$  for "Young's modulus," and  $\mu$  for "Poisson's ratio," as in the preceding articles, the two following relations are known to hold for isotropic bodies:<sup>1</sup>

$$C = \frac{E}{3(1-2\mu)}; \quad T = \frac{E}{2(1+\mu)}.$$

Straubel, by employing these two formulae, has deduced the values given in the last two columns of the following table. The values of  $E$  were taken from the results of Winkelmann and Schott (see Art. 72). In the case of the two glasses 278<sup>III</sup> and 1893, the values were personally communicated by Winkelmann. The values of  $E$  for 2175 and 2106 have not been directly determined; and Straubel adopted for them the values actually found for two other glasses (88 and 24 in Winkelmann's list) which closely resemble them in composition. For 665 there was also no direct determination of  $E$ . Straubel

<sup>1</sup> Thomson and Tait, § 694; Winkelmann, *Handb. d. Phys.*, I. 224.

computed it from Auerbach's values 9094 and 377 for indentation-modulus and hardness, combined with his own determination of  $\mu$ . (See formulae of Art. 77.)

No.	W.	$\mu$	$E$	$C$	$T$
1450	19	·197	7300	4020	3050
278 <sup>III</sup>	—	·208	6640	3790	2750
2175	—	·210	7460	4290	3080
627	87	·213	7970	4630	3290
1893	—	·219	5170	3070	2120
714	91	·221	6570	3920	2690
20	90	·221	6340	3790	2600
2154	86	·222	6100	3660	2500
2106	—	·222	5390	3230	2210
1571	26	·224	5460	3300	2230
709	25	·226	6630	4030	2700
16 <sup>III</sup>	38	·228	7400	4530	3010
2158	28	·231	6610	4100	2690
S. 219	27	·235	6780	4260	2750
500	33	·239	5490	3510	2220
658	21	·250	5470	3650	2190
1973	85	·252	7420	4990	2960
290	30	·253	6010	4060	2400
270	31	·253	6330	4270	2530
370	32	·261	5850	4080	2320
S. 208	20	·261	5090	3550	2020
1299	23	·271	7970	5800	3140
S. 196	22	·274	4700	3470	1840
665	39	·319	8170	7520	3100

Straubel points out that glass 665 is distinguished by its extreme properties;<sup>1</sup> that it shows the greatest hardness, and the largest coefficients of elasticity (including Young's modulus, indentation-modulus, and volume-elasticity), as well as the largest Poisson's ratio; that it has also the smallest thermal expansion; also that it probably has great tenacity and resistance to crushing, great power of withstanding heat, and small electric conductivity.

<sup>1</sup>[No. 665, as the above list shows, is Winkelmann's No. 39. The list of duplicates in Art. 67 shows that No. 39 is identical with No. 11, which is composed of 41 per cent.  $B_2O_3$  and 59 per cent.  $ZnO$ .]

## CHAPTER VIII.

### THERMAL PROPERTIES OF GLASS.

**86.** In this Section, the order of treatment will be: Specific Heat, Conductivity, Expansion, and Power of Withstanding Heat. The experiments which we shall have to describe were performed almost exclusively on the glasses enumerated in Art. 67, where their chemical compositions are described; and we shall designate them by Winkelmann's numbers, there given.

**87. Specific Heats.** The first systematic investigation of the specific heats of glasses of different compositions has been made by Winkelmann, using Regnault's method.<sup>1</sup> Pieces of glass, of an aggregate weight of from 100 to 250 gm., were heated by steam, in a small brass-wire basket, to a temperature  $T^\circ$  near  $100^\circ$ ; and then immersed, with the basket, in a water calorimeter, containing a thermometer and stirrer, and having an initial temperature  $t_1^\circ$ , not differing much from  $14^\circ$ . The final temperature of equilibrium  $t_2^\circ$  was not far from  $18^\circ$ . This temperature  $t_2$  has been lowered by an amount, which we will call  $\Delta t_2$ , by the escape of heat during the time occupied in attaining equilibrium. Let

- $p$  be the mass of the glass (in gm.),
- $c$  the specific heat of the glass,
- $P$  the mass of the water in the calorimeter (in gm.),
- $A$  the water-equivalent of the calorimeter, stirrer, and thermometer.
- $B$  the water-equivalent of the brass-wire basket.

<sup>1</sup> *Ann. d. Phys. u. Chem.*, 49, 401 (1893).



Then we have

$$(pc + B)T + (P + A)t_1 = (pc + B + P + A)(t_2 + \Delta t_2).$$

From this equation  $c$  is to be found, the other quantities having first been determined by observation.

The heating apparatus consisted of three coaxial vertical cylinders, the innermost being provided at both ends with sliding metal plates for opening and closing.

Into it the wire-basket was lowered half-way down, suspended by a silk thread, and having in its centre the bulb of a thermometer graduated to tenths of a degree. Steam was passed through the two intervening spaces between the three cylinders; and after  $2\frac{1}{2}$  hours the indications of the thermometer were sufficiently constant.

The calorimeter was pushed into its place beneath the heating apparatus a long time before the experiment; and with the help of a stirrer, and a thermometer divided to tenths of a degree, its temperature was observed at regular intervals. It thus attained almost exactly the temperature of its surroundings. The weight of the water was determined immediately before the experiment.

The wire-basket with its contents having then been lowered into the calorimeter, observations of temperature were made every 20 seconds, the basket itself being used as stirrer. The temperature of equilibrium  $t_2$  thus found, combined with the observations taken before immersion, gave the means of determining  $\Delta t_2$ , which was about  $\cdot 023$ .<sup>1</sup>

The water-equivalent  $A$  of the brass calorimeter with stirrer and thermometer, was estimated by calculation at  $15\cdot 13$  gm.

Two different baskets were used. One weighed  $24\cdot 23$  gm. Three experiments made with it when empty gave  $2\cdot 184$  as its water-equivalent. The resulting value of the specific heat of brass was  $\cdot 09014$ , the actual specific heat of brass being  $\cdot 093$ . The difference is due to loss of heat from the basket on its way to the calorimeter. This error is allowed for by using the observed value  $2\cdot 184$  for the water-equivalent; a conclusion verified by two experiments, with about 336 gm. of brass in the basket, which, when worked out, gave the correct value of the specific heat of the metal.

<sup>1</sup> See Winkelmann, *Handb.* II., 2, 323.

The second basket weighed 31.77 gm., and its water-equivalent is accordingly to be taken as

$$\frac{2.184 \times 31.76}{24.23} = 2.863.$$

The weight  $P$  of water in the calorimeter was about 500 gm.

In this way determinations were made for 11 glasses, by 3 experiments for each; and then for 7 glasses, by 2 experiments for each. The difference between different determinations for the same glass never reached 1 per cent. The column headed  $c$  in the table of the next article contains the means of these determinations. Winkelmann estimates their uncertainty due to constant sources of error at 0.6 per cent. as a maximum.

### 88. Calculation of specific heats from chemical composition.

If the thermal capacity of a glass were the sum of the thermal capacities of its constituent oxides, its specific heat  $c$  could be calculated by the formula

$$c = \frac{1}{100} \sum p_i c_i,$$

$\Sigma$  denoting "the sum of such terms as,"  $p_i$  the percentage of any oxide, and  $c_i$  its specific heat.

For the first seven oxides of the list in Art. 67, the specific heats were determined by Regnault, for intervals of temperature roughly identical with those employed by Winkelmann. The values published by Regnault<sup>1</sup> are,

	Sp. heat.	Interval.
SiO <sub>2</sub>	.1913	13°—99°
B <sub>2</sub> O <sub>3</sub>	.2374	16°—98°
ZnO	.1248	17°—98°
PbO	.05118	22°—98°
MgO	.2439	24°—100°
Al <sub>2</sub> O <sub>3</sub>	.2074	8°—98°
As <sub>2</sub> O <sub>5</sub>	.1276	13°—97°

The value given for Al<sub>2</sub>O<sub>3</sub> is the mean of Regnault's values for corundum and sapphire, .1976 and .2173.

<sup>1</sup> *Ann. de Chim. et de Phys.* (3), 1, 129 (1841).

No direct determinations are known for the other seven oxides. Winkelmann calculates their specific heats on the basis of Wösty's law that one and the same chemical atom, in its various solid combinations, has always the same atomic heat, and arrives at the following values:

	Sp. heat.
BaO	·06728
Na <sub>2</sub> O	·2674
K <sub>2</sub> O	·1860
Li <sub>2</sub> O	·5497
CaO	·1903
P <sub>2</sub> O <sub>5</sub>	·1902
Mn <sub>2</sub> O <sub>3</sub>	·1661

The atomic weight of oxygen is taken as 16, and its atomic heat in solid combinations as 4·2 (Wüllner's value). For chlorine 35·5 and 6·26 are taken. The following data are also employed:

The atomic weight of barium is 136·8, and the sp. heat of barium chloride, as determined for the interval 14° to 98° by Regnault, is ·08957.

The atomic weight of sodium is 23; the specific heat of sodium chloride between 14° and 99° is ·2140 according to Regnault. The specific heat of sodium has only been determined between -28° and +6°.

The atomic weight of potassium is 39; the sp. heat of potassium chloride between 14° and 99° is ·1729 according to Regnault. The sp. heat of potassium has only been determined between -78° and 0°.

The atomic weight of lithium is 7, and its sp. heat between 27° and 99° is ·9408 according to Regnault.

The atomic weight of calcium is 39·9. Its sp. heat between 0° and 100° is ·1804 by Bunsen's determination. Hence ·2039 is deduced as the sp. heat of calcium oxide. On the other hand, Regnault found ·1642 as the sp. heat of calcium chloride between 23° and 99°; whence the value ·1767 is deduced for the oxide. The mean of the two values is ·1903.

The atomic weight of phosphorus is 31. For the sp. heat of the salt Pb<sub>2</sub>P<sub>2</sub>O<sub>7</sub> between 11° and 98°, Regnault found ·08208; that of the oxide PbO is given above; hence follows ·1789 for the oxide P<sub>2</sub>O<sub>5</sub>. On the other hand, Regnault found ·2283 as

the sp. heat of the salt  $\text{Na}_4\text{P}_2\text{O}_7$  between  $17^\circ$  and  $98^\circ$ ; whence, with the help of the above value for  $\text{Na}_2\text{O}$ , the value  $\cdot 1941$  is deduced for  $\text{P}_2\text{O}_5$ . Lastly, Regnault found  $\cdot 1910$  as the sp. heat of  $\text{K}_4\text{P}_2\text{O}_7$  between  $17^\circ$  and  $98^\circ$ , which, with the above value for  $\text{K}_2\text{O}$ , gives  $\cdot 1975$  for  $\text{P}_2\text{O}_5$ . The mean of the three values is  $\cdot 1902$ .

The atomic weight of manganese is  $54\cdot 8$ . For its sp. heat between  $14^\circ$  and  $97^\circ$ , Regnault found  $\cdot 1217$ ; this leads to  $\cdot 1646$  for  $\text{Mn}_2\text{O}_3$ . Again, Regnault found  $\cdot 1570$  for  $\text{MnO}$  between  $13^\circ$  and  $98^\circ$ ; this leads to  $\cdot 1676$  for  $\text{Mn}_2\text{O}_3$ . The mean of the two is  $\cdot 1661$ .

When Winkelmann compared his observed values for the glasses with the values calculated by the formula at the beginning of this article, from the values of  $c_i$  above adopted for the constituent oxides, he found differences of more than 2 per cent. in the case of the glasses 1, 2, 9, 11, 16. Four of these (1, 2, 11, 16) are distinguished by large percentages of boric acid. Hence he suspected that the sp. heat assigned to  $\text{B}_2\text{O}_3$  in the calculations was too large. To decide the point, a new determination of the sp. heat of boric acid was made, and this confirmed Regnault's result.

But Regnault determined also the specific heats of four salts of boric acid; and Winkelmann deduced from each of these a determination for the acid, with the following results, including the one previously employed:

$\cdot 2374$	from direct observation on boric acid.	
$\cdot 2158$	from the value $\cdot 09046$ for $\text{PbB}_2\text{O}_4$ .	
$\cdot 2153$	$\cdot 1141$	$\text{PbB}_4\text{O}_7$ .
$\cdot 2421$	$\cdot 2197$	$\text{K}_2\text{B}_4\text{O}_7$ .
$\cdot 2252$	$\cdot 2382$	$\text{Na}_2\text{B}_4\text{O}_7$ .

The mean of the five is  $\cdot 2272$ .

Employing this value instead of  $\cdot 2374$ , without changing the values for the other constituents, he obtained the values given in the column headed  $c'$  of the following table. The differences between the observed values  $c$  and the calculated values  $c'$  are given in the next column, expressed as percentages of  $c$ ; they amount on the average to about 1 per cent. The much larger difference for the first glass is probably due to the content of lithium in



the glass being overestimated, as the lithium oxide appears not to have been dry when weighed. The last column contains the

W.	<i>c</i>	<i>c'</i>	<i>c - c'</i>	<i>s</i>	<i>s . c</i>
1	·2318	·2415	- 4·2 %	2·238	·5188
2	·2182	·2192	- 0·5	2·243	·4894
3	·2086	·2080	+ 0·3	2·424	·5056
4	·2044	·2040	+ 0·2	2·480	·5069
5	·2038	·2049	- 0·5	2·370	·4830
6	·1988	·1983	+ 0·3	2·585	·5139
7	·1958	·1964	- 0·3	2·479	·4854
8	·1907	·1888	+ 1·0	2·629	·5013
9	·1901	·1944	- 2·3	2·588	·4920
10	·1887	·1893	- 0·3	2·518	·4751
11	·1644	·1668	- 1·5	3·527	·5798
12	·1617	·1626	- 0·6	2·848	·4605
13	·1589	·1573	+ 0·9	3·070	·4878
14	·1464	·1439	+ 1·0	3·238	·4740
15	·1398	·1379	+ 1·4	3·532	·4938
16	·1359	·1344	+ 1·1	3·691	·5016
17	·1257	·1272	- 1·2	3·578	·4498
18	·08174	·08201	- 0·3	5·831	·4766

products of the specific heats by the densities (from his own determinations). They represent the thermal capacities per unit-volume, and show only a rough approach to constancy.

**89. Observations on the conductivity** of glasses of various compositions were made by O. Paalhorn in the Physical Institute of the University of Jena.<sup>1</sup> The investigation included the 15 glasses numbered 69 to 83 in Winkelmann's list (Art. 67).

The observations were taken with the aid of an apparatus introduced by C. Christiansen<sup>2</sup> under the name of "conducting column," arranged in the form in which Winkelmann used it for his researches on the variability of the conductivity of gases with temperature.<sup>3</sup>

[Conductivity is usually determined by measurement of the temperature-gradient in the conducting body, and of the heat

<sup>1</sup> *Dissertation*, Jena, 1894.

<sup>2</sup> *Ann. d. Phys. u. Chem.*, 14, 23 (1881).

<sup>3</sup> *Ann. d. Phys. u. Chem.*, 29, 68 (1886).

transmitted through it in a given time. The conductivity is then deduced by means of the relation:

$$\text{flux of heat} = \text{gradient} \times \text{conductivity.}$$

The chief peculiarity of Paalhorn's method was that, instead of directly measuring the transmitted heat, he inferred its amount from previous knowledge of the laws of transmission of heat across a layer of air separating two plates at different temperatures. Our account of these experiments and their reduction is very much condensed from the German.]

The conducting column consisted of three copper plates, with two other substances filling the two gaps between them; one of these substances being air and the other the glass to be tested. The copper plates were circular, each of them being 11 cm. in diameter and 1.503 cm. thick, and were gilded. They were placed horizontally one above another; and each of them had a hole bored horizontally in the middle of its thickness for the insertion of a thermometer; these holes being 5.2 cm. deep and 0.6 cm. in diameter. The thermometer for the lowest plate was divided to fifths of a degree from  $-3^{\circ}$  to  $+35^{\circ}$ ; that for the middle plate, to tenths of a degree from  $9^{\circ}$  to  $42^{\circ}$ . For the top plate there were two thermometers, one divided to fifths from  $33^{\circ}$  to  $75^{\circ}$  and the other to tenths from  $69^{\circ}$  to  $100^{\circ}$ . All four were of Jena glass, were of suitable shape, and were compared with a standard thermometer. They all projected from the copper plates on the same side of the column, so that their stems were one above the other.

Between the topmost copper plate and the middle one there was a layer of air of the thickness of either .023458 cm. or .048088 cm., the plates being kept apart by the insertion of three tiny plates of glass about 1 sq. mm. in area, having either the former or the latter thickness.

Between the middle and lowest plate was the glass disc to be tested. It had the same diameter as the copper discs, and was about half a centimetre thick. The transfer of heat between the glass disc and the copper discs, which were pressed against it, was found to be facilitated by covering the plate with a thin layer of glycerine.

The "conducting column" was contained within a sheet-iron box of square section. The central portion of the base of the

box consisted of a brass plate of 16 cm. diameter soldered in. The column stood on this brass plate in such a position that the stems of the thermometers in the three copper plates were in a diagonal plane of the box. The under-side of the brass plate could be kept cool by allowing a jet of water to play against it. In the sides of the box there were glass discs inserted, serving as windows; and in the top there was a round hole filled by a cylindrical brass vessel, whose bottom (made truly plane) rested on the top of the first copper plate, which it exactly fitted. Into this brass vessel steam could be brought from a generator at a sufficient distance.

In addition to the thermometers above mentioned, there were three horizontally placed thermometers inside the iron box, at the level of the middle copper plate, their purpose being to determine the temperature of its surroundings. One had its reservoir close to the column, one midway between the column and a side of the box, and the third in a corner near one of the glass windows. They were divided to whole degrees.

Each experiment began by letting in steam to the brass vessel at the top of the column. As soon as increase of temperature in the middle copper plate appeared, the water jet was allowed to play against the bottom of the brass plate on which the lowest copper plate rested. The highest and lowest copper plates soon acquired their permanent temperatures. The middle plate changed its temperature, first quickly, and then more and more slowly. When it ceased to change, regular readings were begun.

**90. Reduction of the Observations.** Since the temperatures are steady, the middle copper plate receives just as much heat as it gives out. This fact is expressed by the equation

$$L + S = l + \omega + \sigma, \dots\dots\dots(1)$$

$L$  denoting the heat which it receives by conduction.

$S$  " " " " by radiation.

$l$  the heat conducted from it to the lower plate.

$\omega$  its loss by air-contact and radiation to the surroundings of the column.

$\sigma$  the loss by air-contact and radiation from the glass plate.

91. In one experiment, which may be taken as a sample, the following permanent temperatures were observed :

$t_1$	= temp. of top plate =	96.13° C.
$t_2$	„ mid „	58.29.
$t_3$	„ lowest „	13.75.
$t_4$	„ air around column =	20.3.
Thickness of glass plate, 1.075 cm.		
„	air layer,	.048088 cm.

From these were derived by calculation :

$L$	=	4.81	therms per second.
$S$	=	.02318	„
$\omega$	=	.29329	„
$\sigma$	=	.13944	„

Hence  $l$  is found by (1); and by the help of formulae for the transmission of heat across a layer of air, the value 20.156 was obtained for the relative conductivity  $k$  at the temperature  $\frac{1}{2}(t_1 + t_2) = 36.02^\circ$ . This is to be multiplied by the absolute conductivity of air at the temperature of the air layer, which is about .00006, giving .00121 as the absolute conductivity at  $36^\circ$ .

The value finally adopted for the absolute conductivity  $K$  of the glass in question (the lead silicate glass 69) at  $25^\circ$  C. was .001083.

Experiments conducted in the same way gave for glass 79 (a silicate containing soda and zinc oxide) at the same temperature,  $K = .001931$ .

92. Several comparative observations were made by inserting one of two glasses between the first and second copper plates, and the other between the second and third; the formula employed being

$$L = l + \omega, \dots\dots\dots(3)$$

which reduces to

$$\frac{K_1}{d_1}(t_1 - t_2) = \frac{K}{d}(t_2 - t_3) + .000154 \frac{D}{R}(t_2 - t_4)^{1.181}; \dots\dots\dots(4)$$

$K_1$  and  $d_1$  being the conductivity and thickness of the upper glass plate;  $K$ ,  $d$  of the lower;  $D$  the thickness of the middle copper plate;  $R$  the common radius of the plates. For results, see the next article.



**93. Relation to Chemical Composition.** Paalhorn's values for the absolute conductivities (in C.G.S. units) of the glasses which he tested (namely the 15 glasses 69-83 in Winkelmann's list, Art. 67), are given in the following table, under the heading "observed." They are for temperatures not differing much from 25° C.

W.	K in gm. cm <sup>-1</sup> . sec <sup>-1</sup>		Obs. - Calc.
	Observed.	Calculated.	
69	·001083	·001094	- 1 %
70	·001304	·001324	- 2
71=27	·001409	·001406	+ 0
72	·001433	·001379	+ 4
73	·001445	·001572	- 9
74	·001470	·001401	+ 5
75=23	·001610	·001511	+ 6
76	·001650	·001479	+ 10
77	·001832	·001661	+ 9
78	·001861	·001879	- 1
79	·001931	·001954	- 1
80=5	·002267	·002092	+ 8
81	·001938	·001905	+ 2
82	·001972	·002024	- 3
83	·001952	·001954	- 0

Paalhorn adopted, on the basis of these results, a set of coefficients for expressing the absolute conductivity of a glass as a linear function of the percentages of its constituent oxides; and Winkelmann subsequently suggested changes in the coefficients for B<sub>2</sub>O<sub>3</sub>, ZnO, MgO, BaO, which brought the results into closer agreement with observation. The following are the coefficients as thus altered:

SiO <sub>2</sub>	-	·0000220	As <sub>2</sub> O <sub>5</sub>	-	·0000020
B <sub>2</sub> O <sub>3</sub>	-	150	BaO	-	100
ZnO	-	100	Na <sub>2</sub> O	-	160
PbO	-	80	K <sub>2</sub> O	-	10
MgO	-	84	CaO	-	320
Al <sub>2</sub> O <sub>3</sub>	-	200	P <sub>2</sub> O <sub>5</sub>	-	160

These are the coefficients employed in deducing the above values headed "Calculated."

**94. Relative determinations by Isothermals.** W. Voigt, improving on de Sénarmont's plan of exhibiting the unequal conductivity in different directions of crystalline plates, has shown that isothermal lines on the surface of a plate can be made self-recording by covering the plate with a thin coating of pure elaidinic acid to which certain proportions of wax and turpentine have been added. The elaidinic acid has a definite melting point of about  $45^{\circ}\text{C}$ ., and, in solidifying from the melted state, is deposited in minute crystals, which form a remarkably fine and clear line of demarcation.<sup>1</sup> After employing the method for comparing the principal conductivities of a crystal, he adapted it in the following way to the comparison of the conductivities of two isotropic solids, and thus obtained comparisons between three Jena glasses, nearly identical<sup>2</sup> with Winkelmann's 19, 20, 21.

Two equal plates  $ABC$ ,  $CDA$  (fig. 21), of different glasses, each having the form of a right-angled triangle, are cemented

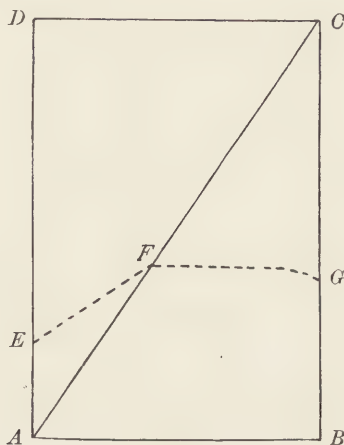


FIG. 21.

together along their hypotenuses, so as to compose a rectangular plate of uniform thickness. The ratio of the length and breadth may with advantage be about the ratio of the conductivities.

The rectangular plate, with a very thin uniform coating of the mixture, is set upright with one end  $AB$  (belonging to the better

<sup>1</sup> Winkelmann, *Handb.*, II. 1, 301.

<sup>2</sup> *Ann. d. Phys. u. Chem.*, 64, 95 (1898).

conductor) resting on an amalgamated block of copper heated to something between  $70^{\circ}$  and  $90^{\circ}$  C. The line of melting  $EFG$  will gradually advance; and when it has attained its permanent position, the angles  $CFG = \phi_1$ , and  $A FE = \phi_2$  are to be measured. If the experiment has been skilfully performed, the two lines  $EF$ ,  $FG$  will be very straight and clear, permitting of determination of the angles to a fraction of a degree. As an uncertainty of  $\frac{1}{4}$  of a degree in the angles entails an uncertainty of about 2 per cent. in the ratio of the conductivities, the method makes a reasonable approach to accuracy.

The line of melting is an isothermal line (having the uniform temperature of the melting point); and the lines of flow of heat are perpendicular to it; hence  $\phi_1$  and  $\phi_2$  are the inclinations of the lines of flow in the two plates to the normal to the surface

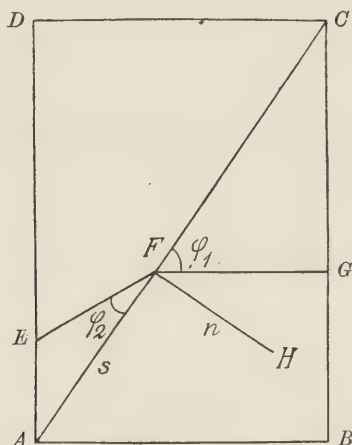


FIG. 22.

of junction (that is to the line marked  $n$  in fig. 22); and, by the general law<sup>1</sup> for change of direction of lines of flow in passing from one isotropic body to another of different conductivity, we have

$$\frac{K_1}{K_2} = \frac{\tan \phi_1}{\tan \phi_2} \dots\dots\dots (5)$$

<sup>1</sup> [Let  $F$  denote the flux of heat at any point of a solid conductor, and  $\phi$  the angle which it makes with the normal to the surface of junction with another conductor. The component flux along the normal is  $F \cos \phi$  and the component flux parallel to the surface of junction  $F \sin \phi$ . The former has the same value

The three glasses were combined two together in each of the three possible ways, the triangles being isosceles, so that the plates were square. Each plate furnished two observations; heat being applied first to the one side and then to the other of the better-conducting triangle. Fig. 23 represents one of the square plates



FIG. 23.

magnified about three times. The lower side and the right side are those to which heat has been applied. The cooling was effected very slowly, and the crystals formed were consequently large. The lines of melting were remarkably fine and sharp; an inadequate idea of their sharpness is given by the representation.

The following were the angles ( $\phi_1$  and  $\phi_2$ ) observed in these six determinations:

19	20	19	21	21	20
44.4°	25.7°	44.8°	36.0°	45.6°	34.8°
49.1°	31.6°	45.1°	37.0°	47.0°	37.1°

on both sides of the junction (otherwise the temperature of the junction would not remain steady); and the latter varies directly as the conductivities (since the temperature-gradient along the junction is common to the two bodies). We have thus the two equations

$$F_1 \cos \phi_1 = F_2 \cos \phi_2; \quad F_1 \frac{\sin \phi_1}{K_1} = F_2 \frac{\sin \phi_2}{K_2};$$

which, by division, give  $\frac{\tan \phi_1}{K_1} = \frac{\tan \phi_2}{K_2}$ .



The values of the ratio  $K_1/K_2$  resulting from these determinations, according to equation (5), are given in the following table; the values headed  $a$  being derived from the upper, and those headed  $b$  from the lower line of the above table.

$K_1 : K_2$	Observed.			Calculated.
	$a$	$b$	$\frac{1}{2}(a+b)$	
19 : 20	2·035	1·877	1·956	1·947
19 : 21	1·367	1·332	1·349	1·355
21 : 20	1·469	1·418	1·443	1·450

$\frac{1}{2}(a+b)$  is the mean of the two directly observed values of the same ratio. The values headed "Calculated" are the values of each ratio as computed from the other two. The agreement is very close.

Using Paalhorn's determination ·002267 of the value of  $K$  for the glass 19 = 5, we derive from the above values of  $\frac{1}{2}(a+b)$ ,

W.	$K$
20	·001159
21	·001680

It is, however, to be remembered that the glasses employed by Voigt (from which the ratios were derived) were not quite identical with Winkelmann's 19, 20, 21.

**95. Isothermal Method extended to 25 Glasses.** More recently Th. M. Focke,<sup>1</sup> on the suggestion and with the assistance of Voigt, has applied the method of isotherms to the 25 Jena glasses numbered (by Winkelmann) 19-33, 38, 86-94. To deduce their absolute conductivities, he determined, by a method which had been suggested by Voigt and employed by O. Venske<sup>2</sup> for some preliminary measurements, the absolute conductivity (which we shall call  $K_0$ ) of a specimen of plate glass, and found it to be

$$K_0 = \cdot 002454.$$

<sup>1</sup> *Ann. d. Phys. u. Chem.*, 67, 132 (1899). Inaug. Dissert. Göttingen.

<sup>2</sup> *Göttinger Nachrichten*, 1892, 121.

Comparisons were made, by the method of isotherms, between this glass (of relatively high conductivity) and each of the 25; also (as a check) between each of the 25 and one of the others.

The double plates were square, and of from 2 to 4 sq. cm. area. They were warmed on a water bath, coated very thinly with shellac, and then with the melted mixture of elaidinic acid and wax. The shellac caused the acid mixture to adhere better. As soon as a plate was coated, it was cooled on a metal stand; the cooling being effected quickly in order that the crystals formed might be small. The plate after cooling was pressed at one of its edges against a block of copper at 60° or 80° C. When the melting had advanced about 4 mm., the plate was removed from the heater and cooled slowly. As the crystals formed during this slow cooling were large, there was a well-marked distinction between the part that had melted and the part that had not.

For measuring the two angles  $\phi_1$ ,  $\phi_2$  (fig. 24) made by the two isothermals with the diagonal, a Norremberg polarisation

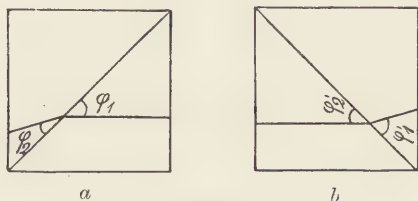


FIG. 24.

apparatus was used, the analyser being replaced by a small telescope with well centred crosswires. The plate was laid on the stage of the apparatus, and illuminated by reflection from a small mirror below. When the flow of heat was from the better conducting half to the worse, the isotherms were nearly straight and the measurement was easy. When it was from the worse to the better conductor, the isotherms were curved and the measurement was more difficult. After some practice, however, it was found possible to make fairly accurate measurements, even in this case.

**Reduction of the Experiments.** Fig. 24 shows the two cases. In case *a*, which we shall call "the first arrangement," the flow of heat across the diagonal has been from the better to the worse conductor. In case *b*, which we shall call "the

second arrangement," its flow across the diagonal has been from the worse to the better conductor.

The first measurements were all made with the first arrangement. In some cases, in which the difference of conductivity was small, both arrangements were employed, and it was found that the second arrangement gave a ratio of greater inequality than the first, the discrepancy averaging about 10 per cent. Also, when two glasses were compared with the standard glass and with each other, the results were generally inconsistent.

For example, glasses 21 and 91 gave

$$K_{21}/K_0 = \cdot 802, \quad K_{91}/K_0 = \cdot 903,$$

giving, by division,

$$K_{21}/K_{91} = \cdot 888,$$

whereas direct comparison gave  $\cdot 798$ .

Attempts to explain and remove these discrepancies<sup>1</sup> were not very successful; and a compromise was made by adopting, instead of  $\tan \phi_1/\tan \phi_2$  given by the first arrangement, or  $\tan \phi_1'/\tan \phi_2'$  given by the second arrangement, the intermediate value

$$\frac{K_1}{K_2} = \frac{\tan \phi_1 + \tan \phi_1'}{\tan \phi_2 + \tan \phi_2'} \dots\dots\dots (6)$$

The **Results** are collected in the following table. The first column gives the designations of the two glasses which compose a double-plate. The second column, headed "Observed," gives the mean values calculated by equation (6). Each set of three consecutive comparisons consists of comparisons of two glasses with the standard, followed by their direct comparison with each other. The discrepancies, if examined, will be found to be small;

[If  $K$  denote the conductivity of the intervening shellac;  $\alpha$ ,  $\beta$  and  $\alpha'$ ,  $\beta'$  the angles made by the isotherm in the shellac with the surfaces of the plates in the two cases; theory gives

$$\frac{\tan \phi_1}{\tan \alpha} = \frac{K_1}{K} = \frac{\tan \phi_1'}{\tan \alpha'},$$

$$\frac{\tan \phi_2}{\tan \beta} = \frac{K_2}{K} = \frac{\tan \phi_2'}{\tan \beta'};$$

whence

$$\frac{K_1}{K_2} = \frac{\tan \phi_1 \tan \beta}{\tan \phi_2 \tan \alpha} = \frac{\tan \phi_1' \tan \beta'}{\tan \phi_2' \tan \alpha'}.$$

It is suggested that, owing to irregularity in the shellac (which showed numerous bubbles), the alternate angles were not equal, but  $\alpha < \beta$ , and  $\alpha' > \beta'$ . The two values obtained for  $K_1/K_2$  would then be unequal. We have omitted fig. 25, which illustrates this point.]

and Focke has smoothed his results by ascribing equal errors to each of the three comparisons. The smoothed values thus obtained are given in the column headed "Calculated." This

Plate	Obs.	Calc.	1000 K	Plate	Obs.	Calc.	1000 K
23.0	0.831	0.832	2.041	94.0	1.015	1.017	2.495
25.0	1.001	1.000	2.458	24.94	0.818	0.819	—
23.25	0.831	0.832	—	26.0	0.816	0.816	2.003
31.0	0.737	0.741	1.819	29.0	0.982	0.981	2.407
87.0	1.062	1.056	2.591	26.29	0.833	0.832	—
31.87	0.846	0.837	—	30.0	0.860	0.867	2.128
21.0	0.850	0.857	2.103	88.0	1.027	1.019	2.499
91.0	0.986	0.978	2.399	30.88	0.859	0.852	—
21.91	0.884	0.877	—	32.0	0.811	0.822	2.016
27.0	0.807	0.805	1.974	38.0	1.008	0.995	2.442
89.0	0.971	0.973	2.387	32.38	0.836	0.826	—
27.89	0.825	0.827	—	33.0	0.698	0.699	1.715
20.0	0.649	0.650	1.595	92.0	1.005	1.002	2.462
90.0	0.968	0.967	2.372	33.92	0.698	0.697	—
20.90	0.673	0.672	—	19.0	1.111	1.105	2.712
22.0	0.780	0.785	1.927	28.0	0.915	0.925	2.269
93.0	0.898	0.904	2.222	28.19	0.846	0.837	—
22.93	0.886	0.880	—	86.0	0.896	0.892	2.189
24.0	0.835	0.833	2.044	86.19	0.804	0.807	—

description does not apply to the last five comparisons in the table, which relate to the last three glasses and have been smoothed by the method of least squares.

The entries in the last column, when divided by 1000, are the absolute conductivities (of the first named glass in the first column). They are found by multiplying the smoothed values by 2.454, which is 1000 times the conductivity of the standard glass.

**Influence of Chemical Composition.** In continuation of Winkelmann's list (Art. 67), the following table is added for the three glasses 92-94:

	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	ZnO	Al <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>5</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Sb <sub>2</sub> O <sub>3</sub>
92	65.9	23.5	—	—	0.8	6.3	—	3.5
93	53.5	20.0	—	—	—	—	6.5	20.0
94	63.37	11.0	12.0	4.0	0.6	9.0	—	—



Focke, in deducing from his results a linear formula for the conductivity of a glass in terms of the percentages of its constituents, obtained the coefficients given in the last column of the following table. The coefficients obtained by Paalhorn and by Winkelmann (see Art. 93), are prefixed for comparison :

Oxide.	Paalhorn.	Winkelmann.	Focke.
SiO <sub>2</sub>	22. 10 <sup>-6</sup>	22. 10 <sup>-6</sup>	31.56. 10 <sup>-6</sup>
B <sub>2</sub> O <sub>3</sub>	16	15	20.02
ZnO	11	10	12.05
PbO	8	8	12.40
MgO	8.2	8.4	37.13
Al <sub>2</sub> O <sub>3</sub>	20	20	25.89
As <sub>2</sub> O <sub>5</sub>	2	2	- 131.7
BaO	11	10	12.59
Na <sub>2</sub> O	16	16	7.03
K <sub>2</sub> O	1	1	5.98
CaO	32	32	9.46
P <sub>2</sub> O <sub>5</sub>	16	16	—
Sb <sub>2</sub> O <sub>3</sub>	—	—	2.82

Focke's coefficients give fair agreement with observation for each of the 25 glasses, as is seen by comparing the column headed "Calculated" in the following table with the preceding column, which contains the observed values. The last column contains the differences (observed — calculated) expressed as percentages.

No.	1000 K	Calc.	Diff.	No.	1000 K	Calc.	Diff.
19	2.71	2.72	- 0 %	32	2.02	2.08	- 3 %
20	1.60	1.62	- 1	33	1.72	1.75	- 2
21	2.10	2.13	- 1	38	2.44	2.48	- 2
22	1.93	1.94	- 1	86	2.19	2.19	0
23	2.04	1.98	+ 3	87	2.59	2.48	+ 4
24	2.04	2.00	+ 2	88	2.50	2.49	+ 0
25	2.46	2.44	+ 1	89	2.39	2.36	+ 1
26	2.00	1.95	+ 3	90	2.37	2.42	- 2
27	1.97	1.97	0	91	2.40	2.49	- 4
28	2.27	2.32	- 2	92	2.46	2.50	- 2
29	2.41	2.42	- 0	93	2.22	2.18	+ 2
30	2.13	2.09	+ 2	94	2.50	2.45	+ 2
31	1.82	1.82	0				

**Comparison with Paalhorn's Values.** In the case of the three glasses 19 (also called 5 and 80, see Art. 67), 23, and 27, direct comparison is possible between Focke's values and Paalhorn's, and is given in the following table. The last column contains their differences expressed as percentages of Paalhorn's values, Focke's values being the larger in every case.

Glass.	Paalhorn.	Focke.	Diff.
19	·002267	·002712	20
23	1610	2041	27
27	1409	1974	40

Besides the large average excess of Focke's values over Paalhorn's (about 30 per cent.), there are large differences in their ratios; for instance,  $K_{19}/K_{27}$  is 1·61 according to Paalhorn, and 1·37 according to Focke. Winkelmann has shown<sup>1</sup> that it is not easy to decide which of the two sets of results is the more correct; and that there may be genuine differences, depending on differences in the temperatures of observation.

**Conductivity and Index of Refraction.** Finally Focke determined for 22 of the glasses the index of refraction for sodium light, and compared them with the conductivities to see if any connection could be found between them. The results were in the main negative, though, on the whole, the worst conductors had the highest indices.

**96. Another way of Computing Conductivity from Chemical Composition.** In place of the mode of computation employed in Art. 93, Winkelmann has recently adopted another with better success. Instead of the percentages by weight  $a_1, a_2, \dots$ , he introduces the percentages by volume  $b_1, b_2, \dots$ , and determines the coefficients  $x_1, x_2, \dots$ , in the formula

$$\frac{1}{K} = b_1 x_1 + b_2 x_2 + \dots \dots \dots (1)$$

for the reciprocal of the conductivity.

Let  $v_1, v_2, \dots$  denote the volumes, and  $z_1, z_2, \dots$  the specific gravities of the constituent oxides in the condition in which they

<sup>1</sup> *Ann. d. Physik u. Chem.*, 67, 794 (1899).

exist in the glass (see Art. 68),  $w_1, w_2, \dots$  being their weights; then we have  $v_1 = w_1/z_1$ ,  $v_2 = w_2/z_2$ , etc., and

$$\frac{b_1}{100} = \frac{v_1}{\sum v} = \frac{w_1/z_1}{\sum (w/z)} = \frac{a_1/z_1}{\sum a/z} \dots\dots\dots(2)$$

Hence  $b_1, b_2, \dots$  can be calculated from the values of  $a$  in Art. 67, combined with the values of  $z$  in Art. 68.

The following values of  $x$  have been deduced by Winkelmann from Paalhorn's observations (Art. 93):

SiO <sub>2</sub> = 3·4	MgO = 5·0	Na <sub>2</sub> O = 10·5
B <sub>2</sub> O <sub>3</sub> = 6·6	Al <sub>2</sub> O <sub>3</sub> = 2·5	K <sub>2</sub> O = 13·3
ZnO = 15·0	As <sub>2</sub> O <sub>5</sub> = 3·0	CaO = 6·0
PbO = 16·0	BaO = 13·0	P <sub>2</sub> O <sub>5</sub> = 6·7

The values of  $K$  obtained by employing these coefficients in the formula (1) for  $1/K$  are given in the following table, under the heading "Calculated"; and they do not show any large departure from the observed values:

W.	K in cm <sup>-1</sup> g sec <sup>-1</sup>		Difference.
	Observed.	Calculated.	Obs. - Calc.
69	0·001083	0·001067	+1 %
70	1304	1361	-4
71=27	1409	1408	+0
72	1433	1495	-4
73	1445	1524	-5
74	1470	1416	+4
75=23	1610	1637	-2
76	1650	1582	+4
77	1832	1764	+4
78	1861	1919	-3
79	1932	1934	-0
80=5	2267	2198	+3
81	1940	1930	+1
82	1972	2037	-3
83	1952	1946	+0

**Derivation of Formula (1).** Winkelmann was led to formula (1) by considerations which may be put in the following shape: let there be any number  $n$  of successive parallel layers

$A$ ,  $B$ , etc. (fig. 26) with steady flow of heat perpendicularly through them. Let their thicknesses be  $d_1, d_2 \dots d_n$ ; their

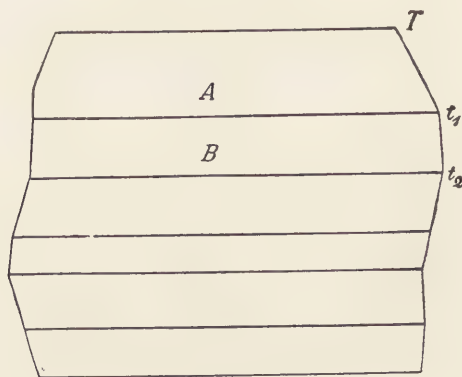


FIG. 26.

conductivities  $K_1, K_2 \dots K_n$ ; the temperatures of their junctions  $t_1, t_2 \dots t_{n-1}$ , and of the first and last surfaces  $T, t$ .

The flux of heat  $F$  per unit area will be the same for all the layers, and is given by

$$F = K_1 \frac{T - t_1}{d_1} = K_2 \frac{t_1 - t_2}{d_2} = \text{etc.} \dots \dots \dots (3)$$

Hence we have

$$T - t_1 = \frac{d_1}{K_1} F; \quad t_1 - t_2 = \frac{d_2}{K_2} F \dots; \quad t_{n-1} - t = \frac{d_n}{K_n} F;$$

and by addition,

$$T - t = \left( \frac{d_1}{K_1} + \frac{d_2}{K_2} + \dots + \frac{d_n}{K_n} \right) F \dots \dots \dots (4)$$

If the layers were replaced by a single uniform layer of the same total thickness  $D$ , and of such conductivity  $K$  as to give the same flux of heat  $F$ , we should have

$$T - t = \frac{D}{K} F.$$

Equating the two values of  $\frac{T - t}{F}$ , we have

$$\frac{D}{K} = \frac{d_1}{K_1} + \frac{d_2}{K_2} + \dots + \frac{d_n}{K_n}, \dots \dots \dots (5)$$



which is equivalent to (1), since  $\frac{d_1}{D}100$  is the volume percentage of the first layer,  $\frac{d_2}{D}100$  that of the second layer, and so on. These being the values of  $b_1, b_2, \dots$ , we must have

$$x_1 = \frac{1}{100 K_1}, \quad x_2 = \frac{1}{100 K_2},$$

and so on.

**97. Coefficient of Cubical Expansion of Glass; and its Dependence on Chemical Composition.** The cubical expansibilities of the glasses 39-68 in Winkelmann's list have been determined by Winkelmann, Straubel, Pulfrich, and Weidmann; and the results have been published by Schott<sup>1</sup> together with the chemical compositions of the glasses. The following table contains the coefficients thus determined. The first column, headed *W*, contains Winkelmann's numbers for the glasses; the second column, headed *B*, the observer's name abbreviated; the third column, headed *M*, indicates the method of observation, *A* denoting the Abbe-Fizeau method,<sup>2</sup> and *D*, Dulong and Petit's method, by filling a glass vessel with mercury.<sup>3</sup> The letters in the next column, headed *K*, indicate the mode of cooling of the glass from the red-hot condition, *O* denoting the cooling-oven, *L* open-air cooling, *R* fine-cooling in the thermo-regulator. The column headed "Interval" gives the initial and final temperatures; and it will be noticed that their mean is, in every case, not far from 50° C. The coefficient of linear expansion being denoted by  $\alpha$ , the coefficient of cubical expansion is  $3\alpha$ , and its values multiplied by  $10^7$  are given in the next column, headed "Observed," the order of arrangement being from the least to the greatest. Schott remarks that the differences are much larger than in the case of ordinary glasses.

There are not many bodies with such small expansibility as the zinc borate glass No. 39; on the other hand the alumina glass No. 68 is nearly as expansible as iron and nickel.

<sup>1</sup> *Vortrag im Verein zur Beförd. d. Gewerbfl. eisses, Berlin, 1892.*

<sup>2</sup> Winkelmann, *Handb.* II. 2, 54.

<sup>3</sup> Winkelmann, *Handb.* II. 2, 48.

Schott has also investigated the dependence of expansibility on chemical composition; and has pointed out the influence of the

W.	B.	M.	K.	Interval.	$3\alpha \times 10^7$		Diff.
					Obs.	Calc.	
39=11	P.	A.	R.	10°·35 - 92°·88	110	110	+ 0 %
40=12	"	"	L.	12°·67 - 89°·78	137	149	- 9
41=21	"	"	O.	7°·16 - 91°·8	157	175	- 11
42	Wd.	"	?	0 - 100	161	162	- 1
43	"	"	R.	"	168	168	+ 0
44=36	W.	D.	L.	"	177	194	- 10
45=2	P.	A.	R.	14°·4 - 94°·4	202	191	+ 5
46	"	"	O.	15°·7 - 92°·2	236	244	- 3
47	"	"	"	12°·9 - 97°·6	238	241	- 1
48	"	"	R.	18°·9 - 93°·1	238	220	+ 8
49	"	"	"	17°·5 - 94°·9	239	240	- 0
50	"	"	O.	19°·8 - 94°·5	241	251	- 4
51=6	"	"	"	14°·6 - 92°·2	241	254	- 5
52	"	"	"	18°·7 - 90°·5	265	272	- 3
53=13	"	"	R.	20°·3 - 92°·2	261	246	+ 6
54	"	"	O.	9°·95 - 93°·3	270	240	+ 11
55	"	"	"	15°·65 - 94°·2	271	263	+ 3
56	"	"	R.	17°·9 - 97°·2	275	254	+ 8
57	"	"	"	17°·7 - 92°·7	279	295	- 6
58=20	"	"	O.	24°·5 - 84°·0	280	256	+ 9
59	W.	D.	L.	0 - 100	290	284	+ 2
60	P.	A.	O.	17°·0 - 95°·5	289	263	+ 9
61	S.	D.	L.	0 - 100	292	314	- 8
62	"	"	"	"	300	294	+ 2
63	"	"	"	"	305	289	+ 5
64	"	"	"	"	305	294	+ 4
65	"	"	"	"	314	327	- 4
66	"	"	"	"	324	319	+ 2
67	P.	"	"	"	328	330	- 1
68	"	A.	O.	17°·8 - 96°·5	337	355	- 5

alkalis in promoting expansibility. He remarks, in connection therewith, that sodium and potassium are highly expansible metals.

Winkelmann and Schott have since published<sup>1</sup> the following coefficients by which the percentages of the constituent oxides

<sup>1</sup> *Ann. d. Phys. u. Chem.*, 51, 735 (1894).

are to be multiplied, in order to obtain, by addition, the value of  $10^7$  times the cubic expansibility  $3a$ :

$\text{SiO}_2 = 0.8$	$\text{BaO} = 3.0$
$\text{B}_2\text{O}_3 = 0.1$	$\text{Na}_2\text{O} = 10.0$
$\text{ZnO} = 1.8$	$\text{K}_2\text{O} = 8.5$
$\text{PbO} = 3.0$	$\text{CaO} = 5.0$
$\text{MgO} = 0.1$	$\text{P}_2\text{O}_5 = 2.0$
$\text{Al}_2\text{O}_3 = 5.0$	$\text{Li}_2\text{O} = 2.0$
$\text{As}_2\text{O}_5 = 2.0$	

The arrangement in order of magnitude, beginning with the largest, is  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{BaO}$ ,  $\text{PbO}$ ,  $\text{As}_2\text{O}_5$ ,  $\text{Li}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{ZnO}$ ,  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{B}_2\text{O}_3$ .

The column headed "Calculated" contains the results of employing the above coefficients in conjunction with the list of percentages in Art. 67, which is taken from the first of the two papers by Winkelmann and Schott mentioned at the beginning of the article. An earlier list published by Schott, in the paper mentioned in Art. 4, shows some slight differences;  $\text{Mn}_2\text{O}_3$  in small quantities not exceeding 0.2 per cent. being given as an ingredient of several of the glasses. Again, in the second of the two papers by Winkelmann and Schott, there is a difference in the case of glass 61, which, instead of 1.5 per cent. of  $\text{Al}_2\text{O}_3$ , is stated to contain 1.5 per cent. of  $\text{B}_2\text{O}_3$ . The calculated value 314 for this glass will be changed to 307 by this substitution.

The last column gives the difference (obs. — calc.) expressed as a percentage of the observed value.

**98. Influence of Stress on Expansibility.** Three of the glasses, Nos. 44, 51, 56, were also tested for expansibility in varying conditions of stress. The quicker a glass is cooled, the greater is the stress left in it after cooling. In his paper, mentioned in Art. 4, Schott expressed the view that, with increasing stress, the coefficient of expansion probably increased also; and adduced the following observations on these three glasses in support of the view.

The largeness of the difference, in the case of glass 56, is attributed by Schott to the circumstance, that the solid glass cylinders, employed in the Abbe-Fizeau observations, had stronger stresses in them than the thin-walled vessels, employed in the

Dulong-Petit method. The rapidly cooled cylinder which gave the value 289 was cut from a glass rod 20 mm. in diameter,

W.	Observer.	Method.	Cooling.	$3a \times 10^7$
44	Winkelmann	Dulong-Petit	Thermoregulator	171
"	"	"	Free air	177
51	Pulfrich	Abbe-Fizeau	Cooling oven	241
"	Winkelmann	Dulong-Petit	Free air	244
56	Pulfrich	Abbe-Fizeau	Thermoregulator	275
"	"	"	(See below)	289

which, after being drawn in the plastic state, was allowed to cool in air. The following is a fuller account of its behaviour, as observed by Pulfrich and quoted by Schott.

Its ends were originally ground perfectly flat, but, after the cylinder had been kept for some time at  $96^\circ \text{C}$ ., were found to be distinctly concave, showing that the thermal expansion parallel to the axis increased from the axis to the circumference. Measurements made at different distances from the axis gave

Distance.	$3a \times 10^7$
0 mm	277
7.5	302
10	327

When the cylinder had cooled down, the ends were still concave. After being again ground flat, they remained flat after three hours' immersion in boiling water; and a determination made in the usual way gave  $3a \times 10^7 = 289$ .

The cylinder, with its ends still plane, being then immersed in oil at  $200^\circ \text{C}$ ., again showed concavity at the ends. The concavity was sensible after five minutes, and after an hour became constant. Similar results were obtained with other glass cylinders.

These experiments show, as Schott remarks, that a permanent small deformation of the elementary portions of the glass is possible at temperatures far below the softening point. Much depends on the composition of the glass. A cylinder of the baryta-



borosilicate (free from alkali) numbered 12 = 40 by Winkelmann, and having the trade number 121<sup>III</sup>, preserved perfectly the planeness of its ends after heating, although it was in a highly stressed condition.

Schott suggests that phenomena of this kind play a part in the change of zero of mercury thermometers, and that they also explain the frequent failure of attempts to make truly spherical vessels of stressed glass.

In previous investigations of the thermal expansibility of glass, no precise information as to chemical composition has usually been given. Regnault, however, in his research on mercury thermometers,<sup>1</sup> gives the percentage composition<sup>2</sup> of the eleven glasses whose expansions he determined. Four of the eleven, though having the same origin and only slight differences in composition, showed considerable differences in expansion. This, as Schott remarks, can be explained by supposing that they had been cooled under different conditions.

### 99. Change of Coefficient of Expansion with Temperature.

For one of the glasses included in Schott's list of Art. 97, namely No. 52, Pulfrich's observations had shown a distinct increase of the coefficient with temperature. He found

Interval.	$3\alpha \times 10^7$
4°·85 to 18°·7	258
18°·7 to 90°·5	265

Fuller observations on the course of thermal expansion in glasses from 0° to 100° have been carried out by M. Thiesen and K. Scheel, and at higher temperatures by E. Reimerdes.

**Course of Expansion from 0° to 100°.** Thiesen and Scheel's observations<sup>3</sup> were taken at the Reichsanstalt, and relate to three glasses used for the construction of high-class thermometers; namely, the French hard glass known as *verre dur*, of which

<sup>1</sup> *Mém. de l'Académie*, 21. 205.

<sup>2</sup> The particulars are given in full in Winkelmann's *Handb. d. Phys.*, II. 2. 62; also in Schott's paper.

<sup>3</sup> *Zeitschr. f. Instrumentenkunde*, 1892. 293.

Tonnello's thermometers are made, and the two Jena thermometer-glasses numbered 44 and 51 in the list of Art. 67.

The *verre dur* had the following composition:<sup>1</sup>

SiO <sub>2</sub> .	MgO.	Al <sub>2</sub> O <sub>3</sub> .	Na <sub>2</sub> O.	K <sub>2</sub> O.	CaO.
70.96	0.40	1.44	12.02	0.56	14.40

The number given for Al<sub>2</sub>O<sub>3</sub> includes oxide of iron as well as alumina. The glass is not very different in composition from ordinary window-glass.

The specimens employed were capillary tubes a little more than 1 m. long and about 5 mm. in external diameter, such tubes as are used in making thermometers. A portion about 1 cm. long at each end was reduced from the cylindrical to the hemi-cylindrical form by grinding away half of it; and the flat surface thus obtained was etched with five divisions half a mm. apart, the central division being about 1 m. distant from the corresponding division at the other end of the tube.

Three series of comparisons were made. In each series one of the tubes was kept at a nearly constant temperature of about 25°, and another tube, at the successive temperatures 0°, 25°, 50°, 75°, 100°, was compared with it. The tubes were kept at these temperatures by floating them in mercury-troughs, each tube being (by means of two corks) held down in immediate proximity to the thermometer which indicated the temperature of the mercury. The actual data of observation are given at length in the published memoir.

For expressing the results, the formula

$$l_t = l_0(1 + at + bt^2)$$

was employed. The mean coefficient of expansion from 0° to  $t^\circ$  is  $a + bt$ , and the true coefficient of expansion at  $t^\circ$  is  $a + 2bt$ .

The first calculations of the values of  $a$  and  $b$  were affected by the circumstance that the periodic errors of the micrometer screws had not been determined. A recalculation, after this want had been supplied, led to the following values, which are taken from a communication bearing the names of Thiesen, Scheel, and Sell.<sup>2</sup> The first table is applicable when  $t$  is

<sup>1</sup> *Ber. d. Berliner Akad.*, 12 Nov., 1885; see Art. 111.

<sup>2</sup> *Wissensch. Abhandl. der Reichsanstalt*, 2. 73 (1895); also *Zeitschr. f. Instrum.*, 16. 54 (1896).

expressed in degrees of the mercury thermometer of Jena normal glass 16<sup>III</sup>. The second table is applicable when  $t$  is in degrees of the hydrogen thermometer.

MERCURY THERMOMETER OF GLASS 16<sup>III</sup>.

Mark	W.	$10^3 a$	$10^3 b$
59 <sup>III</sup>	44	565.5	0.272
16 <sup>III</sup>	51	768.9	.387
<i>Verre dur</i>	—	738.5	.390

## HYDROGEN THERMOMETER.

Mark	W.	$10^3 a$	$10^3 b$
59 <sup>III</sup>	44	568.0	0.245
16 <sup>III</sup>	51	772.3	.350
<i>Verre dur</i>	—	741.7	.355

For the cubic expansions of the three glasses, there results

$$v_t = v_0(1 + At + Bt^2)$$

with  $A = 3a$  and  $B = 3(a^2 + b)$ , giving, for the mercury-thermometer scale,

Mark	$10^3 A$	$10^3 B$
59 <sup>III</sup>	1696.4	0.828
16 <sup>III</sup>	2306.6	1.181
<i>Verre dur</i>	2215.4	1.189

and for the hydrogen scale,

Mark	$10^3 A$	$10^3 B$
59 <sup>III</sup>	1703.9	0.746
16 <sup>III</sup>	2316.7	1.071
<i>Verre dur</i>	2225.2	1.083

It may be assumed that these values of expansibility include the thermal after-effect [Nachwirkung], as the rods were maintained

for a considerable time at the temperatures of observation before the temperatures were taken.

**Normal Expansion and Principal Expansion.** In the nomenclature adopted by Thiesen, Scheel, and Sell,<sup>1</sup> the whole expansion from  $0^\circ$  to  $t^\circ$  is made up of two parts: the principal expansion and the after-effect; so that if  $At + Bt^2$  is the full amount of expansion when sufficient time is allowed for the after-effect to be completed (called the *normal* expansion), and if  $A't + B't^2$  is the after-effect, then  $(A - A')t + (B - B')t^2$  is the *principal* expansion [Hauptausdehnung]. The constants  $A - A'$  and  $B - B'$  are to be employed instead of  $A$  and  $B$  for computing the expansions which accompany *sudden* changes of temperature.

Employing for the three thermometer-glasses the values of  $A'$  and  $B'$ , given in next chapter (Art. 114), we obtain, for the interval  $0^\circ$ — $100^\circ$ ,

FOR HYDROGEN THERMOMETER SCALE.

Mark	W.	$10^8(A - A')$	$10^8(B - B')$
59 <sup>III</sup>	44	1695.8	0.770
16 <sup>III</sup>	51	2306.5	1.022
Verre dur	—	2209.3	1.068

We may so far anticipate as to say that the determination is made by comparing the volume after cooling to  $0^\circ$  with the original volume at  $0^\circ$ .

**Expansion of Glass from  $40^\circ$  to  $220^\circ$ .** The investigation carried out by Reimerdes<sup>2</sup> related to the three glasses with the trade names, O. 802, O. 627, O. 1552. Their chemical compositions, which are here given, differ little, if at all, from those of the glasses 5, 49, 28 of Winkelmann's list (Art. 67); so they may also be designated by these numbers.

Mark	W.	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	ZnO	Al <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>5</sub>	BaO	Na <sub>2</sub> O	K <sub>2</sub> O	Mn <sub>2</sub> O <sub>3</sub>
O. 802	5	70.83	14.0	—	5.0	0.1	—	10.0	—	0.07
O. 627	49	68.24	10.0	2.0	—	0.2	—	10.0	9.5	0.06
O. 1552	28	64.72	2.7	2.0	—	0.5	10.0	5.0	15.0	0.08

<sup>1</sup> *Zeitschr. f. Instrum.*, 16. 50 (1896).

<sup>2</sup> *Ausdehnung des Quarzes*. Dissertation, Jena, 1896.



The Abbe-Fizeau method was employed; but instead of the usual table with screw feet, which was found unsuitable, a quartz ring was used as the comparison body. It was therefore necessary, as a preliminary to the principal measurements, to determine the course of expansion for the quartz ring. The determination of this, from the temperature of the room up to  $230^{\circ}$ , forms therefore the first part of the record. The mean linear coefficient  $a$  for each glass was then determined for four (in the case of glass 49 for five) partial intervals of temperature, lying between the extremes  $40^{\circ}$  and  $220^{\circ}$  or thereabouts.

Constancy of temperature was maintained by means of a thermostat of the d'Arsonval construction filled with linseed oil, its indiarubber membrane being replaced by a steel diaphragm. Its performance was at first very good, but was gradually impaired by repeated and long-continued heating to above  $200^{\circ}$ ; and in the later observations on the glasses it did not afford sufficient security for the desired constancy. An element of uncertainty was thus introduced into the measurements. From the values of  $a$  obtained directly from the observations, the values of  $a$  and  $b$  in the formula

$$a = a + 2bt$$

were deduced. The results are contained in the following table:

	W.	$10^8a$	$10^8b$	$t$	$10^8a$		Diff.
					Obs.	Calc.	
O. 802	5	510.4	0.482	$34^{\circ}81$	527	527.2	- 0.2
				$92^{\circ}33$	552	554.9	- 2.9
				$148^{\circ}95$	586	582.2	+ 3.8
				$212^{\circ}09$	612	612.6	- 0.6
O. 627	49	724.9	1.010	$38^{\circ}99$	764	764.8	- 0.8
				$55^{\circ}10$	782	780.6	+ 1.4
				$94^{\circ}91$	826	820.7	+ 5.3
				$151^{\circ}25$	879	877.7	+ 1.3
				$217^{\circ}45$	937	944.6	- 7.6
O. 1552	28	887.9	1.103	$37^{\circ}36$	920	929.2	- 9.2
				$92^{\circ}91$	1004	990.4	+ 13.6
				$151^{\circ}12$	1061	1054.6	+ 6.4
				$212^{\circ}34$	1111	1122.1	- 11.1

Each temperature in the column headed  $t$  is the mean tem-

perature of the interval to which the number standing opposite to it in the next column (headed "Observed") belongs. The numbers under the heading "Calculated" are derived from the formula  $a + 2bt$ .

**100. Compensation Vessels.** Schott has pointed out that it is possible, by suitably combining an outer containing vessel of high expansibility with an inner displacing vessel of low expansibility, to obtain compensation of expansions, so that the remaining volume is independent of temperature.

Let  $v_1$  be the capacity of the containing vessel,  
 $v_2$  the volume of the displacer,  
 $a_1, a_2$  their coefficients of linear expansion.

Then the simultaneous increments of  $v_1$  and  $v_2$  for a small rise of temperature will be as  $a_1 v_1$  to  $a_2 v_2$ ; and if these increments are equal, the remaining volume will be unchanged. The condition to be fulfilled may be written

$$\frac{v_1}{a_2} = \frac{v_2}{a_1} = \frac{v_1 - v_2}{a_2 - a_1},$$

the constant volume being  $v_1 - v_2$ .

By reversing this arrangement—that is, by making  $a_1$  greater than  $a_2$ , the changes in the remaining volume  $v_1 - v_2$  can be exaggerated, and may even be made so great as to compensate the expansion of a contained liquid. The condition for this, if  $\gamma$  denote the coefficient of expansion of the liquid, is

$$3a_1 v_1 - 3a_2 v_2 = \gamma(v_1 - v_2)$$

or,

$$\frac{v_1}{\gamma - 3a_2} = \frac{v_2}{\gamma - 3a_1} = \frac{v_1 - v_2}{3a_1 - 3a_2}.$$

A suitable combination for either of these purposes would be 102<sup>III</sup> with 59<sup>III</sup> or 121<sup>III</sup>, or, in Winkelmann's numbering, 68 with 44 or 40.

**101. Compound Glass** [Verbundglas]. In discussing the unequal expansions of different glasses, Schott, in his paper of 1892,<sup>1</sup> gave some information respecting compound glass. Experiments were made to ascertain how two glasses of different

<sup>1</sup> Vortrag im Verein z. Beförd des Gewerbf., 4 April, 1892, p. 11.

expansibilities behave when one is superposed upon the other in the blowing, so as to give a glass composed of two dissimilar layers. The results showed that certain received views are only true with a qualification.

"It has been an accepted rule with glass makers that, when an article is built up of portions of material taken separately out of the melting pots, all the portions must be of similar composition, and if possible from the same pot. In the cases in which it is necessary to unite two glasses of different composition—for instance, in making glasses with coloured coatings, or glass tubes with streaks of white enamel, care is taken to employ two kinds which have as nearly as possible the same expansibility, in order to prevent the product from flying to pieces in cooling."

"Some trials which I made for the purpose of deciding whether two glasses of different expansions, if joined by laying one over the other at the pipe, will always fly to pieces in cooling, showed that the view hitherto prevalent is not altogether correct. It was soon demonstrated that, by fulfilling certain conditions, it was possible to unite even glasses with considerable differences of expansibility. The main condition concerns the relative thicknesses of the two glasses."

Let  $A$  and  $B$  be two kinds of glass, with linear coefficients of expansion  $\alpha$  and  $\beta$ ,  $\alpha$  being the greater. If they are welded together when hot, so as to form two layers of a single plate, then, when the plate has cooled,  $A$  will be in tension, and  $B$  in thrust. If the double layer is drawn out into a thread, the thread, as it cools, curls up, with  $A$  on the inside.

In general, the intensities of the stresses in a compound glass are difficult to specify. They depend, not only on the coefficients  $\alpha$  and  $\beta$ , but also on the moduli of elasticity and Poisson's ratios of the two glasses, on the thicknesses of the two layers, and on the form and dimensions of the vessel composed of them. The vessel will fly to pieces if the tension in  $A$  exceeds the tensile strength of  $A$ , or if the thrust in  $B$  exceeds the power of  $B$  to resist crushing. As power to resist crushing is much greater than power to resist pull, the layer  $A$  is generally the one that breaks down; and to prevent this, it should be made thicker than the layer  $B$ . For example, if  $A$  is the "normal thermometer glass" 16<sup>III</sup>, and  $B$  the thermometer glass 59<sup>III</sup>, so that



$3\alpha = 241 \times 10^{-7}$ ,  $3\beta = 177 \times 10^{-7}$ , a tube or hollow vessel made of the compound glass, with  $A$  outside and  $B$  inside, should have the layer  $A$  from 10 to 15 times as thick as the layer  $B$ , to be secure against flying to pieces in cooling.

If a lump of glass is heated till it is soft, and then quickly cooled, the outside solidifies while the interior is still soft. The subsequent complete cooling will produce thrust in the outer layer, just as cooling produces thrust in the layer  $B$  of the compound glass. Every layer in a state of thrust, no matter how produced, will necessarily exhibit an enhanced power of resisting pull; as well as greater power of resistance both to scratching and to sudden cooling. The well-known properties of the so-called *toughened glass* [Hartglas] fulfil this anticipation. A layer in thrust—in whichever way produced—may therefore be called a *toughened layer*.

When a lump of glass, by quick cooling, has covered itself with a toughened layer, the interior of the mass must be in a state of extension. Experience shows that, in quickly cooled hollow vessels, the inner surface is in tension. Such a vessel behaves as if it were of compound glass with  $A$  inside and  $B$  outside.

A layer in tension, however produced, behaves in the opposite way to a toughened layer. Its power of sustaining pull is diminished, and a slight scratch or sudden chill suffices to make it give way and to shatter the whole vessel. The so-called *Bologna phial* is the most familiar instance. A glass layer in this condition of permanent tension may very well be called a *sensitive layer* [Sprengschicht].

Adopting these designations, we may say that the resisting power of glass vessels against mechanical and thermal disturbances is increased by covering them with *toughened* layers, and diminished by covering them with *sensitive* layers.

In accordance with the above principles, there are two different ways of completely toughening glass vessels. One way is, to employ a compound glass  $A . B$ , putting the less expansive layer  $B$  inside, and to toughen the outside by rapid cooling in air. In carrying out this plan, uniform cooling of the whole surface is essential; any considerable inequality of stress in the surface being an element of danger. The second plan is, instead of toughening the outer layer  $A$  by quick cooling, to cover it with



a layer of smaller expansibility. The difficulty here is to make this outer layer thin enough.

Schott has shown that both methods can be carried out, and has applied the first to the making of boiling-flasks, beakers, lamp chimneys, and water-gauge tubes for steam boilers. He states that the boiling-flasks, when heated till aniline boils violently in them (boiling point  $184^{\circ}$  C.), may be safely sprinkled with a fine jet of cold water; that the beakers can, without any protection, be heated over a Bunsen flame without cracking; and that the lamp chimneys, while doing duty over an Argand burner, can be sprinkled inside with water without breaking.

It may seem strange that a toughened glass is able to bear abrupt heating on one surface, seeing that such heating increases the thrust already existing in the toughened outer layer. To understand the reason, it must be borne in mind that, when a glass originally free from stress is suddenly heated on one surface, the effect is twofold: a toughened layer is formed on the surface to which heat is applied, and a sensitive layer on the other; and it is this other surface that gives way, because power to resist compression is many times greater than power to resist extension.

**Compound Glass Tubes.** Of the applications of compound glass which have been introduced subsequently to this first announcement, the most important is the construction of water-gauge tubes for steam boilers. Glass tubes which have been so slowly cooled as to be free from stresses cannot be used for this purpose; for the heating of their inner surfaces by the water of the boiler converts their outer surfaces into sensitive layers, which would give way on the contact of a drop of cold water and would be even endangered by a draft of air. On the other hand, tubes merely toughened externally by quick cooling, if not excessively thin, have an extremely sensitive layer at their inner surfaces. The compound glasses with both surfaces toughened, introduced by Schott,<sup>1</sup> satisfy in a high degree the requirements of practice. Their power of withstanding changes of temperature is so great that they may be heated in oil to  $200^{\circ}$  or  $230^{\circ}$ , and immediately plunged upright into cold water, without flying. According to tests made at the Reichsanstalt, they may be sprinkled with drops of cold water when their internal tempera-

<sup>1</sup> German patent 61573.

ture is 200°. Another good quality is, that they are only in the very slightest degree liable to be chemically attacked by hot water, as the inner layer consists of the thermometer glass 59<sup>III</sup>, which has very great power of resisting the action of water.

Compound tubes of this kind are also found serviceable for combustion tubes; as they can stand great pressure, and may, without preliminary heating, be played upon by the flame of a blast furnace.

**102. Power of Withstanding Inequality of Temperature. Coefficient of Thermal Endurance.** If a homogeneous piece of glass, free from stress, is suddenly subjected to changes of temperature which do not extend to its whole substance, stresses are produced which are liable to become so great as to cause fracture. Experience has shown that different glasses have very unequal powers of withstanding such changes.

Winkelmann and Schott have investigated, both theoretically and experimentally, a practically important case.<sup>1</sup>

Let a massive lump of glass be raised throughout to a temperature  $\Theta_1$ , and then immersed in a liquid whose temperature is 0° or at least is taken as the zero of reckoning. The temperature  $\Theta_1$  is taken higher and higher till the glass cracks on immersion. It is required to find the relation of this critical value of  $\Theta_1$  to other properties of the glass. The following investigation may guide us in the inquiry.

Suppose a very thick plate of glass, bounded by an infinitely extended plane face, and having the uniform temperature  $\Theta_1$ , to have this plane face suddenly reduced to the temperature  $\Theta_0$  at the time  $t = 0$ , and permanently maintained at this lower temperature. Let  $\Theta$  denote the temperature in the glass at distance  $x$  from the surface at any subsequent time  $t$ . Then [according to Lord Kelvin's integral of Fourier's differential equation, Thomson and Tait, II. p. 474] the value of  $\Theta$  is given by

$$\Theta - \Theta_0 = (\Theta_1 - \Theta_0) \frac{2}{\sqrt{\pi}} \int_0^m e^{-\beta^2} d\beta, \dots\dots\dots (1)$$

$m$  denoting  $\frac{1}{2}x\sqrt{\frac{sc}{Kt}},$

<sup>1</sup> *Ann. d. Phys. u. Chem.*, 51, 730 (1894).

$K$  being the conductivity,  $s$  the density, and  $c$  the specific heat of the glass.  $\beta$  is a mere numeric which disappears on putting in the limiting values.

For our purpose, only small values of  $t$  and of  $x$  come into consideration, and it is possible, for any assigned value of  $t$ , to choose  $x$  so small that  $m$  is small. Expanding  $e^{-\beta^2}$  and integrating between the limits, we see that, for small values of  $m$ , the integral is sensibly equal to  $m$ . Writing  $m$  for it, equation (1) becomes

$$\Theta - \Theta_0 = \frac{2m}{\sqrt{\pi}} (\Theta_1 - \Theta_0). \dots\dots\dots(2)$$

We shall assume that the tension produced in the surface is proportional to

$$aE (\Theta - \Theta_0),$$

and therefore to  $aEm (\Theta_1 - \Theta_0)$ ,

that is, to  $aE \frac{x}{\sqrt{t}} \sqrt{\frac{sc}{K}} \cdot (\Theta_1 - \Theta_0)$ ,

$E$  denoting Young's modulus and  $a$  the coefficient of linear expansion for the glass.

In comparing two glasses, if we take  $x$  and  $t$  the same for both, the tensions in their surfaces will be the values of

$$B aE \sqrt{\frac{sc}{K}} \cdot (\Theta_1 - \Theta_0),$$

$B$  being a constant, the same for both. Fracture will occur if the difference of temperature  $\Theta_1 - \Theta_0$  is sufficiently great to make this tension exceed the tenacity  $P$  of the glass in question. The limiting difference of temperature is therefore

$$\Theta_1 - \Theta_0 = \frac{1}{B} \cdot \frac{P}{aE} \sqrt{\frac{K}{sc}} \dots\dots\dots(3)$$

Winkelman and Schott accordingly adopt

$$F = \frac{P}{aE} \sqrt{\frac{K}{sc}} \dots\dots\dots(4)$$

as the measure of *power to withstand inequality of temperature*, and call it the *thermal coefficient of endurance* [thermischer Widerstandskoeffizient].

If the coefficient of cubic expansion were written in the denominator instead of the coefficient of linear expansion,  $F$

would be divided by 3. The following list of calculated values of  $\frac{1}{3}F$  for the 20 glasses numbered 19 to 38 in Winkelmann's list (Art. 67) has been published by Winkelmann and Schott. The values of the elements employed in the calculation are also given.

W.	<i>P</i>	$10^3\alpha$	<i>E</i>	$10^3K$	<i>s</i>	<i>c</i>	$\frac{1}{3}F$
19 = 5	6.95	183*	7296	2.267	2.370	0.204	3.56
20	3.53	280	5088	1.080*	5.944	0.079*	1.17
21	6.12	157	5474	1.544*	2.758	0.169*	4.10
22 = 2	5.76	202	4699	1.572*	2.243	0.218	3.45
23	7.52	195*	7952	1.610	3.532	0.138*	2.79
24	6.07	250*	5389	1.365*	3.578	0.125*	2.49
25	8.51	249*	6498	1.946*	2.572	0.201*	3.23
26	5.39	248*	5467	1.323*	3.879	0.118*	2.14
27	5.56	295*	6780	1.409	2.588	0.189*	1.49
28	6.76	265*	6626	1.689*	2.580	0.179*	2.32
29 = 8	6.79	263*	6514	1.905*	2.629	0.191	2.45
30 = 10	7.82	368*	6014	1.605*	2.518	0.189*	2.05
31 = 13	7.63	261	6296	1.440*	3.070	0.159	2.51
32	8.32	313*	5862	1.404*	2.668	0.178*	2.47
33	5.32	252*	5512	1.188*	4.731	0.096*	1.96
34	8.16	183*	7001	2.004*	2.378	0.206*	4.06
35 = 7	8.35	226*	7077	2.157	2.479	0.196*	3.48
36	7.73*	177	7260	2.040*	2.370	0.205*	3.90
37 = 12	7.75*	137	7232	1.729*	2.848	0.162*	4.84
38 = 6	9.06*	241	7543	2.100	2.585	0.199*	3.18

Those marked with an asterisk were not directly observed, but computed from the chemical composition of the glasses in accordance with formulæ which we have given in previous articles. The column headed *E* contains the values denoted by  $E_1$  in Art. 72, except in the case of glass 30, for which  $E_2$  is given. The column headed *P* gives the maximum observed values of tenacity of Art. 69. The last column contains the values of  $\frac{1}{3}F$ , computed from the six elements *P*,  $3\alpha$ , *E*, *K*, *s*, *c*. Reference to the units employed in the articles from which these elements are quoted will show that the unit for  $\frac{1}{3}F$  is cm. sec.<sup>- $\frac{1}{2}$</sup> .

**103. Experimental Tests of Thermal Endurance.** Winkelmann and Schott made experimental tests of withstanding power for inequality of temperature in the case of 13 different glasses.



Polished cubes of the glasses were heated in water, or (when temperatures above  $100^{\circ}$  were required) in glycerine, and then suddenly immersed in cold water, to ascertain the greatest difference of temperature they could bear without cracking. The trials showed that the more the difference of temperature exceeded that which could just be borne, the greater was the number of cracks produced.

For 5 cubes of 2 cm. edge of glass 21, the following results were obtained. With a difference of temperature of  $94^{\circ}\cdot 8$ , three of the five were uninjured, and the other two showed a few cracks. The three then bore a difference of  $96^{\circ}\cdot 8$ ; but one of them when tested with a difference of  $111^{\circ}$  showed a very few cracks. The other two bore a difference of  $103^{\circ}\cdot 5$ , and then of  $108^{\circ}$ . One of them bore  $110^{\circ}\cdot 5$ , but the other when subjected to the same difference showed a few cracks. The difference  $110^{\circ}\cdot 5$  was therefore adopted as the maximum for this kind of glass. Difficulties presented themselves very similar to those which were encountered in the determination of tenacity; slight defects in the surface of a glass being found to produce very considerable diminution of its withstanding power.

The following table shows the results thus obtained for the 13 glasses; the values of  $\frac{1}{3}F$  (from the table of Art. 102) being reproduced for comparison. They are arranged in descending order of  $F$ .

W.	$\frac{1}{3}F$	$\Theta_1$ for Cube whose edge is	
		2 cm.	1 cm.
21	4·10	$110^{\circ}\cdot 5$	$148^{\circ}\cdot 0$
34	4·06	—	$148^{\circ}\cdot 0$
19 = 5	3·56	$95^{\circ}\cdot 5$	—
22 = 2	3·45	$84^{\circ}\cdot 7$	$103^{\circ}\cdot 5$
25	3·23	$78^{\circ}\cdot 5$	$103^{\circ}\cdot 5$
23	2·79	$70^{\circ}\cdot 9$	$90^{\circ}\cdot 5$
31 = 13	2·51	$32^{\circ}\cdot 0$	$50^{\circ}\cdot 5$
24	2·49	$66^{\circ}\cdot 2$	$98^{\circ}\cdot 5$
28	2·32	$77^{\circ}\cdot 8$	$88^{\circ}\cdot 4$
26	2·14	$69^{\circ}\cdot 8$	$88^{\circ}\cdot 5$
33	1·96	$65^{\circ}\cdot 8$	$87^{\circ}\cdot 0$
27	1·49	—	$62^{\circ}\cdot 7$
20	1·17	$52^{\circ}\cdot 8$	$61^{\circ}\cdot 9$

As stated in the early part of Art. 102,  $\Theta_1$  denotes the difference between the temperature of the cold water in which the glass was immersed, and the temperature of the glass immediately before immersion. It is to be presumed that the temperature of the cold water was the same within  $1^\circ$  or  $2^\circ$  in all the experiments; and assuming this to have been the case, the order of arrangement for  $F$  should also be the order of arrangement for  $\Theta_1$ . A glance shows that the order is on the whole the same; but there are some irregularities near the middle of the list, especially as regards glass 31, whose large departure from regularity the observers were not able to explain. It is, however, to be remembered that many of the elements employed in calculating the values of  $\frac{1}{3}F$  were not furnished by direct observation (see the asterisks in the table of Art. 102), and very precise agreement could therefore scarcely be expected.

It will be noted that in every case the cube of 1 cm. edge was able to bear a greater difference of temperature than the cube of 2 cm. edge. This, as Winkelmann and Schott remark, is in accordance with the familiar fact that the thinner a glass is, the better is it able to bear exposure to sudden changes of temperature.

104. In connection with the question of the greatest difference of temperature between itself and a liquid in which it is to be immersed that a body can bear without cracking, it is pertinent to inquire what difference of temperature it can bear between the surface layer and its interior.

If a body, raised to temperature  $\Theta_1$ , has its surface so rapidly cooled to temperature  $\Theta_0$  that only a relatively very thin layer has changed its temperature at the time when cracking occurs, we may assume that the tension at the surface is a function of the difference of temperature  $\Theta_1 - \Theta_0$ . When the body is a sphere, this tension and its maximum value can be easily calculated.

105. The surface layer of the sphere, being at temperature  $\Theta_0$ , and surrounding an internal sphere of temperature  $\Theta_1$ , is in the same conditions of stress as a thin spherical shell whose internal volume has undergone the expansion  $3a(\Theta_1 - \Theta_0)$  in consequence

of internal pressure against the shell. The ordinary formulæ<sup>1</sup> for the case give, when the shell is indefinitely thin,

$$p = a(\Theta_1 - \Theta_0) \frac{E}{1 - \mu}, \dots\dots\dots (1)$$

$p$  denoting the tension produced in the shell,  $E$  Young's modulus, and  $\mu$  Poisson's ratio.

If we assume that the shell will be ruptured when  $p$  exceeds the tenacity  $P$ ; then, for the maximum difference of temperature, we have,

$$\Theta_1 - \Theta_0 = (1 - \mu) \frac{P}{aE} \dots\dots\dots (2)$$

It is, however, to be noticed that the pull applied to an element of the surface layer is not, like the pull on a prismatic rod in determinations of tenacity, a pull in one direction only, but in all tangential directions equally. It can be resolved into two pulls in directions perpendicular to one another. As each of these two pulls has the intensity  $p$ , the tenacity as measured by the maximum value of  $p$  will be considerably smaller than the tenacity as usually understood.

In the following table for the 13 glasses of Art. 103, the

W.	$\mu$	$P$	$10^3 a$	$E$	$\Theta_1 - \Theta_0$
21	0.250	5.66	157	5471	148°
34	0.201*	7.92	183*	7090	146
19 = 5	0.197	6.76	160	7296	140
22 = 2	0.274	4.93	202	4802	111
25	0.226	7.84	249*	6632	110
24	0.232*	6.01	250*	5389	103
23	0.271	7.21	195*	7972	102
31 = 13	0.253	7.42	261	6334	101
33	0.239	4.97	252*	5494	82
26	0.224	4.67	248*	5464	80
28	0.231	6.09	283	6613	75
27	0.235	5.46	295*	6780	63
20	0.261	3.28	280	5088	51

values of the maximum difference  $\Theta_1 - \Theta_0$ , as calculated from equation (2), are given in the last column, arranged in order of

<sup>1</sup> Von Lang, *Theoret. Physik* (1891), S. 515.

magnitude. The other columns contain the elements used in the calculation. The values of  $\mu$  are taken, with two exceptions, from Straubel's determinations (Art. 85). For  $P$  the mean values given in Art. 69 are selected (not the maximum values as in some previous tables), and even these are too large, for the reason above stated. The values of  $\alpha$  are the same as in Art. 102, except that Reimerdes' determinations are adopted for 19 and 28. The values of  $E$  are the means of  $E_1$  and  $E_2$  of Art. 72, except that for glass 19  $E_1$  is given. All numbers marked with asterisks are values which have not been directly observed, but computed from the chemical composition of the glasses. The errors in these may have slightly deranged the order of succession of the values of  $\Theta_1 - \Theta_0$ .

#### 106. Effects of Surface Conduction. Fourier's equation

$$H\Theta_0 = K \left( \frac{d\Theta}{dx} \right)_{x=0}$$

which expresses that the heat communicated from the surface of the body to the surrounding medium is equal to that conducted through the surface layer, suggests that steepness of the temperature-gradient  $\frac{d\Theta}{dx}$  is promoted by large values of the surface conductivity  $H$ . As steepness of gradient is one of the factors tending to produce rupture, it is possible that the low withstanding power of glass 31 (Art. 103), which appeared to conflict with theory, may be due to exceptionally good surface conduction in this glass. It is also possible that there may have been in some cases unequal surface conduction at different parts of the surface of one and the same cube. Such inequality would obviously tend to promote fracture, and it is more likely to occur in the case of large cubes than of small ones.

#### 107. Endurance of Sudden Heating.

When a massive piece of glass, initially at atmospheric temperature, is suddenly immersed in a hot bath, its surface is thrown into a state of thrust, and its inner portion into a state of tension. It is to be expected that the difference of temperature which can be borne in these circumstances will far exceed that which can be borne



when the difference is in the opposite direction; for the stress at the surface is in both cases far more intense than the opposite stress of the inner portion, and strength to resist thrust is far greater than strength to resist pull.

Winkelmann and Schott, after giving expression to these views, confirmed them by a striking experiment.<sup>1</sup> No. 20, the last glass in the list of Art. 103, is conspicuous for the smallness of its power to withstand sudden cooling; its 2 cm. cubes could only bear a difference of  $52^{\circ}8$ . A cube of this glass of the same size, when tested by immersion in melted tin, showed itself able to bear a sudden elevation of temperature of  $465^{\circ}$  without cracking.

### 108. Application to Laboratory Uses and Lamp Chimneys.

In the Jena Works, certain glasses, distinguished by their power of withstanding sudden changes of temperature, are employed for the construction of vessels for use in chemical and physical laboratories, and also for chimneys to protect incandescent gas lights.

**Laboratory Glass** [Gerätéglass]. The glass used for flasks, beakers, retorts, and evaporating dishes, is thoroughly tested for its behaviour under sudden cooling and heating. Flasks of moderate size will usually bear dipping in cold water when they contain boiling toluidin, which has a temperature of  $200^{\circ}$  C.

Winkelmann and Schott<sup>2</sup> have published a detailed account of results obtained in the use of these vessels; the following are some of the items:

Beakers, without the protection of wire-gauze, could be heated by a Bunsen burner, or by several such burners, for raising cold water to the boiling point, and keeping it boiling.

A much severer test is furnished by the Fletcher blast-flame. To this intensive source of heat 68 different vessels were exposed.

13 of them were boiling-flasks of 3.3 to 0.5 litre capacity.

24 were Erlenmeyer conical flasks of 1.1 to 0.2 lit.

31 were beakers of 3.6 to 0.2 lit.

In all these vessels, without wire-gauze or other protection, cold water was heated; and only two of the 68 cracked, these

<sup>1</sup> *Ann. d. Phys. u. Chem.*, 51. 745 (1894).

<sup>2</sup> *Zeitschr. f. Instrumentenkunde*, 14. 6 (1894).

two being beakers of about 1 lit. capacity. By a Fletcher blast-flame a litre of water was raised in 3.3 minutes from 12° to boiling. The same operation occupied 11 minutes with a simple Bunsen burner; no wire-gauze being employed in either case. A much longer time is occupied when wire-gauze is used. The following observations relate to a beaker of 10 cm. diameter containing 1 litre of water.

Without wire-gauze.		With wire-gauze.	
Minutes.	Temperature.	Minutes.	Temperature.
0	11°0	0	10°5
6	61	6	36.5
11.3	boil.	12	59.2
		18	78.9
		24	92.5
		28.6	boil.

With the saving of time there is a corresponding saving of gas. To raise a litre of water from 13° to boiling in a beaker of 10 cm. diam. required 74.0 litres of gas when wire-gauze was used, and only 30.5 when it was dispensed with. To maintain a litre of water in ebullition in a beaker of 10 cm. diam. required a consumption of 2.6 litres of gas per minute with, and 1.1 litre without wire-gauze. Dispensing with wire-gauze thus effects a saving of 60 per cent. in time and 58 per cent. in gas.

**Chimneys for Incandescent Gaslight.** Several accounts have been published of the properties of Jena glass chimneys. We may refer especially to three papers in Schilling's *Journal for Gas Lighting and Water Supply*, 1895, from which the following are extracts. We may premise that the Jena chimneys are of two kinds of glass, designated "Green-stamp" and "Gold-stamp."

Müller says: "Having heated the cylinder by using it with an Auer burner, I touched its hottest zone with a stick of ice, and it did not crack. I then repeated the experiment over a Siemens-Kranz burner, with the same result.

"To test its ability to withstand draughts, I then blew cold air from a pump against the hottest zone, without injury. I then repeated the experiment with air compressed, first to two and then to three atmospheres, with the same negative result.

"I next dipped the cylinder in water and placed it, dripping

wet, over an Auer burner, which I immediately lighted. The water went off in steam, but the cylinder remained unbroken. When all the water had evaporated, and the cylinder had become hot, I sprinkled water upon it with a brush. Eleven cylinders of different kinds of glass, including the Bacharat glasses, gave way immediately under this treatment, but all the gold-stamp cylinders remained uninjured. A green-stamp cylinder broke in two after being five times sprinkled with cold water. The experiment was repeated several times, both with the same cylinders over again, and with other Jena cylinders taken promiscuously out of stock.

"To see how far the endurance of the gold-stamp cylinders could be carried, they were then taken hot from the burner and immersed in cold water. This was done in three different ways. First, they were entirely submerged quickly, then slowly, and thirdly they were slowly immersed for half their height. Every specimen stood these tests, though some were tested three or five times in succession.

"I then inclined the burner and chimney from the vertical at angles of  $30^\circ$ ,  $40^\circ$ ,  $50^\circ$ ,  $60^\circ$ , and  $80^\circ$ , and in each case sprinkled the chimney abundantly with cold water. All the Jena cylinders stood this test, except one specimen of "green-stamp," which at an inclination of  $30^\circ$  gave way at the fourth sprinkling.

"Further, the same experiments were repeated with a damaged incandescent mantle. It had a hole 14 mm. wide at the top, and also a slit 12 mm. wide running from top to bottom. The cylinders stood this test also."

Further trials with a damaged mantle, however, showed, as was anticipated, that the cylinders were not able to bear a pointed flame playing for a long time on one place.<sup>1</sup> The intimation issued by the makers relates to the endurance of the cylinders in the normal use of incandescent gas lights, and not to abnormally severe experiments.

Finally, Muchall tested the relative merits of glass and mica cylinders for incandescent lights, 538 burners being fitted with mica cylinders instead of glass. The result showed a small saving in mantles, but a loss of light, besides a great inferiority from the aesthetic point of view.

<sup>1</sup>"Laboratory glass" also is unable to bear a pointed flame directed for a length of time on one spot.

He goes on to say: "In the meantime some trials were made with various glass cylinders composed of separate pieces joined together, but no especially satisfactory result was obtained. Further experiments in this direction would be superfluous; as for some months past ordinary glass cylinders of really astonishing endurance have been supplied by the Jena Works. These cylinders, while in actual use over the burner, can be sprinkled with cold water without cracking." . . . "Here, in Wiesbaden, out of 22 street lamps (of the candelabrum kind) in one street, which were fitted with these new cylinders on the 22nd of December<sup>1</sup> as a test, now, after the lapse of four weeks, not one has yet cracked, though the weather has been unusually trying with rain, wind, and snow."

<sup>1</sup>1894.



## CHAPTER IX.

### AFTER-WORKING AND THERMOMETRY.

**109. After-working in Thermometer Bulbs.** If a newly-made thermometer is left to itself, and merely exposed to variations of atmospheric temperature, the glass, which acts as containing vessel for the mercury, gradually contracts. The end of the mercurial column accordingly gives continually higher indications for one and the same actual temperature. The progress of the change can be traced by observing the freezing point from time to time in an ice bath. It is found that the slow rise of indication, usually called *secular rise of zero*, becomes continually slower as time goes on.

On the other hand, this creeping-up can at any time be interrupted by raising the thermometer to a high temperature, and cooling it quickly, but not suddenly. By this treatment the capacity of the containing vessel is increased, and the freezing point is accordingly lowered. This action, which we shall have frequent occasion to refer to, we shall designate *depression of zero*. If the thermometer is then again left to itself, this depression is gradually cancelled by renewed rising of zero.

*The depression of zero which can be produced in a given thermometer by raising it to 100° and cooling it with the proper quickness is called the **depression-constant** of the thermometer.* It does not attain its permanent value till the thermometer is old. The depressibility before this stage is reached is smaller, and its increase is more and more slow till the permanent maximum of depressibility is attained.

A new thermometer can be "aged" artificially by keeping it

for a long time at a high temperature—for example, at  $100^{\circ}$ —and then cooling it with extreme slowness. This raises the zero, and at the same time increases the depressibility.

If a thermometer is maintained for a long time at a temperature a little over  $250^{\circ}$ , and then allowed to cool without special precautions, its zero will be considerably raised and its depressibility will in general be diminished.

**110. Weber's Investigation of the Influence of the Composition of the Glass on the Depression-Constant.** The very comprehensive observations of R. Weber on this point were published in 1883.<sup>1</sup> They were performed upon 23 different thermometers, of which some were made from commercial tubing, and some from tubing specially provided for the purposes of experiment. The chemical compositions of all were determined by analysis. The scales of the thermometers were divided to tenths of a degree in the neighbourhood of the zero-point, and the intervals were large enough to admit of subdivision by estimation.

After careful determination and marking of their zero-points, with every precaution to ensure accuracy, they were left to themselves for  $1\frac{1}{2}$  or 2 months. After the lapse of this time the new positions of the zeros were noted. The thermometers were then immersed for 15 minutes in boiling water, and thence transferred to the ice bath, in which another observation of their zeros was made. These operations were repeated several times at intervals of at least some months.

Very conspicuous differences were found between glasses of different compositions. At the time of these experiments, it was very usual to make thermometers of soft and easily fusible glasses, containing no lead, and rich in alkalis. Weber's No. 1 thermometer was of a very light and fusible Thuringian glass; and the results which it gave are here reproduced, together with its percentage composition. The column headed *D* contains the values of the depression-constant at each date, the final value being nearly half a degree. Leaving out of account glasses which were not old enough to admit of a determination of the constant with certainty, most of the glasses which Weber tested showed large depressions.

<sup>1</sup> *Ber. d. Berlin. Akad.*, Dec. 13, 1883.

## THERMOMETER OF THURINGIAN GLASS.

Made June 5, 1878.

SiO <sub>2</sub> .	Na <sub>2</sub> O.	K <sub>2</sub> O.	CaO.	Al <sub>2</sub> O <sub>3</sub> .
68·30	12·08	8·27	10·41	1·28

Date of Observation.	Freezing-point.		D
	Before boiling.	After boiling.	
1878, Oct. 23	+0°·497	+0°·095	0°·402
79, May 17	·507	·064	·443
81, Jan. 27	·65	·20	·45
81, July 22	·60	·27	·33
82, May 22	·66	—	—
83, June 7	·65	—	—
83, Oct. 31	·68	·20	·48

A decidedly better result was given by thermometer No. 13, made from "an old tube of uncertain origin."

## THERMOMETER No. 13.

Made June 5, 1878.

SiO <sub>2</sub> .	Na <sub>2</sub> O.	K <sub>2</sub> O.	CaO.	Al <sub>2</sub> O <sub>3</sub> .
65·00	0·07	19·51	13·58	2·04

Date of Observation.	Freezing-point.		D
	Before boiling.	After boiling.	
1878, Oct. 23	+0°·072	-0°·015	0°·087
79, May 17	·069	- ·043	·112
81, Jan. 27	·11	+ ·01	·10
81, July 22	·10	+ ·01	·09
82, May 22	·10	—	—
83, June 7	·10	—	—
83, Oct. 31	·10	·00	·10

With the view of obtaining a larger quantity of glass of this last kind, experimental meltings were undertaken.

The first melting, with the formula

SiO <sub>2</sub> .	Na <sub>2</sub> O.	K <sub>2</sub> O.	CaO.	Al <sub>2</sub> O <sub>3</sub> .
65·73	—	19·15	13·26	2·18

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proved disappointing. The thermometer No. 14 made of it had, at the end of two years, a depression-constant  $0^{\circ}36$ . Closer examination showed that the glass was not homogeneous. Further meltings were therefore made with larger quantities, but these also were unsuccessful. On analysis it was found that the intention to exclude soda had been defeated by the employment of impure potash.

By using chemically pure potash, two glasses were produced having the compositions

$\text{SiO}_2$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{CaO}$	$\text{Al}_2\text{O}_3$
65.42	—	19.46	13.67	0.93
69.04	—	18.52	13.21	0.89

and two thermometers (Nos. 19 and 20) were made of them on Aug. 18, 1883. On Oct. 31, they both showed a total rise of zero amounting to  $0^{\circ}11$ , and a depression-constant  $0^{\circ}09$ . Weber sums up the results of his investigations by saying:

"The depression-constant is largely dependent on the composition of the glass. The very fusible alkali glasses, which on account of their easy working have been much employed, give bad results. A good result is given by pure potash glasses with large proportions of silicic acid and lime."

**111. Further Investigations of After-working and its Relation to Chemical Composition** were undertaken jointly by the Berlin Standards Commission<sup>1</sup> and the Jena Glass Laboratory. An account of the results has been given by H. F. Wiebe.<sup>2</sup>

**Analysis of Glasses of known Depression-quality.** In the first instance, analyses were made at Jena of the glass of seven thermometers, belonging to the Standards Commission, for which the depression-constants were very exactly known. Before the determination, the thermometers had been lying idle for at least a year; and in making the determinations, they were kept at the boiling point for about an hour.

The results of the analysis confirmed and completed Weber's conclusions. It was clear that largeness of depression depended

<sup>1</sup> Normal-Aichungs-Kommission.

<sup>2</sup> In three papers: I. *Ber. d. Berlin. Akad.*, 17 July, 1884; II. *Ibid.*, 12 Nov., 1885; III. *Zeitschr. f. Instrum.*, 6. 167 (1886). In the following articles these papers are referred to as I., II., III.



mainly on the proportions of alkalis in the glasses. A glance at the following extract from Wiebe's table<sup>1</sup> shows that the depression  $D$  is greatest in those glasses which contain soda and potash in about equal proportions; that when the proportions are unequal, no material difference in  $D$  results from interchanging them; and that the smallest  $D$  is for a potash glass nearly free from soda. The percentage of lime ranges from 7 to 14 for the glasses in our list.

Designation of Thermometer, and when made.	Na <sub>2</sub> O	K <sub>2</sub> O	$\frac{\text{Na}_2\text{O}}{\text{K}_2\text{O}}$	$\frac{\text{K}_2\text{O}}{\text{Na}_2\text{O}}$	$D$
Humboldt No. 2 (before 1835)	0.86	20.09	.04	—	0°.06
J. G. Greiner $F_1$ (1848) - - -	1.48	18.89	.08	—	.15
J. G. Greiner $F_2$ (1856) - - -	3.75	17.14	.22	—	.38 <sup>2</sup>
J. G. Greiner $F_3$ (1872) - - -	16.89	3.56	—	.21	.38
Ch. F. Geissler No. 13 (1875) -	15.35	3.97	—	.26	.40
G. A. Schultze No. 3 (1875) -	16.15	3.95	—	.24	.44
Rapps Nachf. $F_4$ (1878) - - -	12.72	10.57	—	.83	.65

The analysis of English standard-thermometer glass (called *crystal*) gave 33.90 per cent. of lead-oxide with only 49.49 of silicic acid, and only 1.20 of lime. The percentages of alkali, tabulated as above, with the depression, were:

Na <sub>2</sub> O.	K <sub>2</sub> O.	Na <sub>2</sub> O/K <sub>2</sub> O.	$D$ .
1.54	12.26	.13	0°.15

Wiebe<sup>3</sup> gives a little over 0°.2 as the average value of the depression-constant for the lead-containing crystal glass extensively used in England.

In France, in Regnault's time, the chief glass for thermometers was apparently the crystal glass manufactured at Choisy le Roi, which was probably nearly the same as the English glass. Some years previous to the investigation which we are describing, Tonnelot of Paris began to make thermometers of a tolerably

<sup>1</sup> I. 847.

<sup>2</sup> This number is not quite certain, as the thermometer had a paper scale; and it was ascertained later (III. 168) that such scales affect the determination of depression.

<sup>3</sup> III. 170.

pure soda glass (*Verre dur*), which does not differ much in composition from ordinary window glass.<sup>1</sup> The figures were:

$\text{Na}_2\text{O}$ .	$\text{K}_2\text{O}$ .	$\text{K}_2\text{O}/\text{Na}_2\text{O}$ .	$D$ .
12.02	0.56	.05	0°008

The presence of potash is doubtless due to impurity in the soda employed. Lime runs up to 14.40 per cent.

**Results of New Meltings.** With the view of attacking synthetically the problem of the connection between chemical composition and thermal after-working, about 30 different mixtures were melted at the Jena Works, and thermometers made of the glasses so produced were tested by the Standards Commission. The results for 17 of these glasses, divided for convenience of description into three groups, are given below:

## GROUP A.

No.	$\text{SiO}_2$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{CaO}$	$\text{Al}_2\text{O}_3$	$D$
IV	70	—	13.5	16.5	—	0°08
VIII	70	15	—	15	—	0.08
XXII	66	14	14	6	—	1.05
XXXI	66	11.1	16.9	6	—	1.03
17 <sup>III</sup>	69	15	10.5	—	5	1.06
20 <sup>III</sup>	70	7.5	7.5	15	—	0.17

## GROUP B.

No.	$\text{SiO}_2$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{CaO}$	$\text{Al}_2\text{O}_3$	$\text{PbO}$	$\text{ZnO}$	$\text{BaO}$	$\text{Li}_2\text{O}$	$\text{B}_2\text{O}_3$	$D$
II	24	7	—	—	16	—	—	53	—	—	0°02
V	54	—	16	—	—	—	30	—	—	—	.09
VII	51	—	—	—	1.8	3.7	27.7	—	6.5	9.3	.10
IX	63	15	—	8	—	10	—	—	—	4	.08
X	46	8	—	—	—	—	—	40	—	6	.09
XI	65	—	18	—	5	—	—	—	—	12	.09
XIX	50	15	—	—	—	—	20	15	—	—	.07
XXIII	57	8	—	20	10	—	—	—	—	5	.10

<sup>1</sup> II. 1025; see Art. 99.

## GROUP C.

No.	SiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	ZnO	B <sub>2</sub> O <sub>3</sub>	D
14 <sup>III</sup>	69	14	—	7	1	7	2	0°·05
16 <sup>III</sup>	67·5	14	—	7	2·5	7	2	0°·05
18 <sup>III</sup>	52	—	9	—	—	30	9	0°·05

The thermometers were not all of the same age; and to make the determinations of the depression-constant  $D$  as nearly comparable as possible, the new instruments were artificially "aged" in the manner described in Art. 109.

Group A illustrates the action of soda, potash, lime, and alumina. It establishes, beyond question, the general principle that good thermometer glass ought only to contain one alkali—either soda free from potash, or potash free from soda. As a qualification of this principle, it appears, from a comparison of XXII. with 20<sup>III</sup>, that by the addition of lime it is possible to prevent large depression, even in the very unfavourable case of equal quantities of soda and potash. Alumina exercises this restraining influence to nearly the same extent as lime.

In Group B, besides the five oxides in Group A, five others are introduced: PbO, ZnO, BaO, Li<sub>2</sub>O, B<sub>2</sub>O<sub>3</sub>. In none of the glasses of this group does the depression-constant exceed 0°·10; and in the case of the glass II., which contains 53 per cent. of baryta, it is only 0°·02.

Passing from experimental meltings to the requirements for a practical thermometer glass; it is necessary to consider not only smallness of after-working, but other properties, such as facility of working, durability, and absence of colour. Taking these properties into account, the practical outcome of the investigation is exhibited in Group C, which contains three glasses 14<sup>III</sup>, 16<sup>III</sup>, 18<sup>III</sup>, suitable for general thermometric requirements, and having a depression-constant of only 0°·05.

**The Actual Selection.** The only one of these three that has been practically adopted for thermometers is 16<sup>III</sup>; it has been made in large quantities for this purpose at the Jena Works since 1885, under the name *Normal-thermometer glass*. The glass 18<sup>III</sup> promised well at first, inasmuch as thermometers

made of it agreed well with the air-thermometer up to  $50^{\circ}$ ; but it did not behave well in the operations of glass blowing. It was difficult to make into good tubes; and when it was subjected to reheating, fine needle-like pieces crystallised out of it. Its use was therefore renounced.

Fresh experimental meltings were then undertaken, and they resulted in the adoption of the borosilicate glass 59<sup>III</sup>.

Schott published a short account of these further researches.<sup>1</sup> He gives the following comparison between 59<sup>III</sup> and 63<sup>III</sup>:

	SiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>3</sub>	D
59 <sup>III</sup>	72	11	—	—	5	12	—	0°·02
63 <sup>III</sup>	73·2	18·5	—	8·0	—	—	0·3	·05

Our figure 72 for SiO<sub>2</sub> includes the small quantity 0·05 of oxide of manganese, which Schott gives separately.

The two depression-constants given under *D* were for new thermometers, and are therefore not to be regarded as final. Wiebe, who undertook the thermometric testing of these glasses, estimated the permanent values which the depression-constant would attain in course of time, at  $0^{\circ}\cdot03$  to  $0^{\circ}\cdot04$  for 59<sup>III</sup>, and  $0^{\circ}\cdot07$  to  $0^{\circ}\cdot09$  for 63<sup>III</sup>.

The borosilicate glass 59<sup>III</sup> has thus rather smaller after-working than the members of Group C. It also possesses (in common with 18<sup>III</sup>) the advantage of giving mercury thermometers which agree well with the air thermometer up to  $50^{\circ}$ . It is also distinguished by the smallness of its expansion, its cubic coefficient being  $177 \times 10^{-7}$ . Tubes of this glass, as well as of the normal-thermometer glass, are accordingly regularly made at the Jena Works for the construction of thermometers.

**Resistance-glass.** A glass recently introduced by Greiner and Friedrichs of Stützerbach, and now regularly supplied by them under the name of *resistenzglas*—distinguished (as its name indicates) for its power of withstanding chemical attack and sudden changes of temperature—has also come into use as a thermometer glass. Five thermometers made of it were tested

<sup>1</sup> *Zeitschr. f. Instrum.*, 11. 334 (1891).



for depression-constant by Fr. Grützmacher<sup>1</sup> at the Reichsanstalt. The depression observed was from  $0^{\circ}07$  to  $0^{\circ}10$ . A depression of practically the same amount, namely  $0^{\circ}09$ , was subsequently observed in other instruments of the same glass. The thermometers were too new to give certainty as to their permanent depression-constant. The thermometric qualities of the resistenz-glas are considered by Grützmacher to be nearly identical with those of the *verre dur* employed by Tonnelot. The makers describe it as a tolerably pure soda glass.

**Baryta-borosilicate 122<sup>III</sup>.** In the account in Art. 98 of Pulfrich's experiments on the after-working exhibited by stressed glass cylinders when subjected to long-continued heating, it was mentioned that a cylinder of the baryta-borosilicate 121<sup>III</sup>, although under severe stress, did not exhibit these effects. Schott,<sup>2</sup> in commenting on these observations, expressed the opinion that this glass would make mercury thermometers in which change of zero would be very small. It is No. 12 = 40 of Winkelmann's list,<sup>3</sup> and the table in Art. 97 shows that, with one exception (a zinc borate), it had the smallest coefficient of expansion of all the glasses examined.

Another glass, made at Jena, very similar to it in composition, was numbered 122<sup>III</sup>. Four thermometers made of this were tested by Grützmacher at the Reichsanstalt,<sup>4</sup> and found to have depression-constants of only  $0^{\circ}01$  to  $0^{\circ}02$ . It must be added that baryta-borosilicate, being a very hard glass, is very difficult to work.

**112. General Characteristics of Different Thermometer Glasses.** Thus far our comparisons of glasses have been restricted to one feature—the magnitude of the “depression-constant” (Art. 109). It remains to indicate the connection between the values of this constant and the general behaviour of the glasses, as brought out by Wiebe's comparative observations.

**Recovery from Depression.** The thermometers included in Group C of last article recovered so quickly from the small

<sup>1</sup> *Zeitschr. f. Instrum.*, 15. 261 (1895).

<sup>2</sup> *Verh. des Vereins z. Beförd. des Gewerbfl.*, April 4, 1892.

<sup>3</sup> See Art. 67.

<sup>4</sup> *Zeitschr. f. Instrum.*, 15. 262 (1895).

depressions there specified, that, after two or three days, they had regained their original zero readings. The French thermometers tested by Wiebe gave almost as good a result. The thermometers of English glass took about a month to halve their depressions. The thermometers of Thuringian glass, though seventy years old, took on the average from four to six months to regain their original zeros.<sup>1</sup>

**Secular Rise.** The observations on the slow rise of zero in thermometers left to themselves, showed a close connection between this phenomenon and the depression-constant  $D$ . The following table gives the elevation of zero after the lapse of the stated number of days:

Glass.	$D$	Number of Days Elapsed.															
		4	21	42	49	66	88	135	160	175	200	242	285	317	447	570	1450
14 <sup>III</sup>	0°·05	—	—	—	—	0·02	—	—	—	—	—	0·03	—	0·04	—	—	—
16 <sup>III</sup>	0·05	—	—	—	—	—	0·04	—	—	—	—	—	0·04	—	—	—	—
18 <sup>III</sup>	0·05	—	—	—	—	—	—	—	—	—	0·04	—	0·05	—	—	—	—
French Gl.	0·07	—	—	—	0·02	0·04	—	—	—	—	0·07	—	—	—	—	—	—
Engl. Gl.	0·18	—	—	—	—	—	0·10	0·12	—	—	—	—	—	0·15	0·16	—	—
Thur. Gl.	0·36	—	—	—	—	—	—	—	—	—	0·25	—	—	—	—	0·38	0·43
IV.	0·08	—	—	—	—	—	—	—	—	—	—	—	—	0·06	—	—	—
VIII.	0·08	—	—	—	—	—	—	—	—	—	—	—	—	0·06	—	—	—
20 <sup>III</sup>	0·17	—	—	—	—	—	0·13	—	—	—	—	—	—	—	—	—	—
XXII.	1·05	0·05	—	0·09	0·12	—	0·16	—	0·25	0·25	—	—	—	—	—	—	—
17 <sup>III</sup>	1·06	—	—	0·22	—	0·33	—	—	—	—	—	—	0·43	—	—	—	—
XXXI.	1·03	0·24	0·42	—	—	—	—	0·53	—	—	—	—	—	—	—	—	—

The list includes 12 glasses; the first three constitute Group C of last article, and the last six Group A. The thermometers of Thuringian glass were six or seven months old; the others were new. The elevations given are, in each case, the means derived from simultaneous observations of two or more instruments. The glasses IV., VIII., 20<sup>III</sup> are not included in Wiebe's table; but he states subsequently<sup>2</sup> that in thermometers made of 20<sup>III</sup> the elevation after 3½ months was 0°·13, and that thermometers made of IV. and VIII. showed only half this elevation after the lapse of a year.

<sup>1</sup> II. 1024.<sup>2</sup> II. 1027.

It may be added<sup>1</sup> that in thermometers of 63<sup>III</sup> the elevation after six weeks was 0°·03 or 0°·04.

**Artificially Aged Thermometers.** Wiebe gives finally<sup>2</sup> the results of the artificial ageing described in Art. 109. By keeping the instruments at 100° for the number of hours stated, and then cooling them with the greatest possible slowness, the following elevations of zero were produced:

Glass.	<i>D</i>	Time at 100°	Elevation of zero.
14 <sup>III</sup> - -	0°·05	7 hours.	0°·02
16 <sup>III</sup> - -	·05	7 „	·01
18 <sup>III</sup> - -	·05	7 „	·01
French Glass	·07	8 „	·05
English Glass	·18	9 „	·16
20 <sup>III</sup> - -	·17	8 „	·15

In a number of new instruments of Thuringian glass, maintenance for 26 hours at 100° raised the zero by 0°·26, and three days at 100° raised it by 0°·40. One thermometer of glass 59<sup>III</sup> had its zero raised 0°·06 by maintenance for 12 hours at 100°. A second thermometer of the same glass, whose bulb before filling had been subjected to the “fine-cooling” process, had its zero raised only 0°·01 or 0°·02 by keeping it for 12 hours at 100°.

**First Comparison with Air Thermometer.** To complete his tests of the fitness of various glasses for the construction of thermometers, Wiebe made preliminary comparisons of various mercury thermometers with the air thermometer.<sup>3</sup> The following table of results will give an idea of the relative behaviour of

Temperature.	Correction for Reducing to Air Thermometer.					
	14 <sup>III</sup>	16 <sup>III</sup>	18 <sup>III</sup>	Thuringian.	French.	English.
0°	0°·00	0°·00	0°·00	0°·00	0°·00	0°·00
10	-0·01	-0·01	+0·01	-0·03	-0·02	+0·03
20	-0·07	-0·05	-0·02	-0·11	-0·06	0·00
30	-0·08	-0·07	-0·02	-0·12	-0·05	+0·02
40	-0·04	-0·05	+0·01	-0·08	-0·02	+0·09
50	+0·01			-0·05		+0·14

<sup>1</sup> Schott, *Zeitschr. f. Instrum.*, 11. 334 (1891).

<sup>2</sup> II. 1023.

<sup>3</sup> II. 1024.

the glasses named. They were obtained by comparison with a standard mercurial thermometer whose relation to the air thermometer was known. Glass 18<sup>III</sup> gives the best agreement, and Thuringian and English the worst. The positive sign in the case of the English glass is a special feature. It is very unusual to find the mercury thermometer below the air thermometer between 0° and 100°.

The values for Thuringian glass are mean values for the kinds chiefly used. The chemical characters of the French glass (Tonnelot thermometers) and the English (crystal) are described in the preceding article.

The following data for thermometers of glasses 59<sup>III</sup> and 63<sup>III</sup> have been published by Schott.<sup>1</sup>

CORRECTIONS FOR REDUCING TO AIR THERMOMETER.

	59 <sup>III</sup> .	63 <sup>III</sup> .
0°	0°·00	0°·00
10	- 0 ·01	- 0 ·06
20	- 0 ·02	- 0 ·10
30	- 0 ·01	- 0 ·11
40	- 0 ·01	- 0 ·11
50	+ 0 ·02	- 0 ·12

As no information is given respecting the mode of determination, it is not clear whether these results are comparable with those given above.

### 113. Depression as a Function of the Higher Temperature.

A closer insight into the phenomenon of depression is obtained by determining the position of the freezing point on the scale of the thermometer, as a function of the temperature to which the thermometer is raised before immersion in the ice bath. For the Jena normal-thermometer glass, this has been done by A. Böttcher,<sup>2</sup> in the course of a comparison of new and old thermometers belonging to the Reichsanstalt.

The new thermometers were made by R. Fuess from Jena glass, and bore the numbers 245, 246, 247; the old ones numbered 50 and 20 were of Thuringian glass, and a thermometer of English crystal (No. 1115) was also included. For several weeks previous to the trials—and in the case of Nos.

<sup>1</sup> *Zeitschr. f. Instrum.*, 11. 334 (1891).

<sup>2</sup> *Ibid.*, 8. 409 (1888).



50, 1115, for several months,—the thermometers had been lying idle at the temperature of the room.

The comparisons were made at every fifth degree from  $0^{\circ}$  to  $100^{\circ}$ . The thermometers were kept for about two hours at the temperature stated when this was below  $60^{\circ}$ , and for about one hour when it was above  $60^{\circ}$ .

Below  $60^{\circ}$  the temperature was maintained by immersion in a water bath. After immersion for a quarter of an hour, a preliminary observation of the freezing points was made in an ice bath. The thermometers were then transferred back to the warm bath, and at the end of the allotted period the decisive observations of their freezing points were made.

At the temperatures from  $60^{\circ}$  to  $100^{\circ}$ , the thermometers were immersed in the vapours of suitably selected liquids, and the freezing points were only observed at the end of the immersion.

The results of these experiments are given in the two following tables, the zero-point readings denoted by  $E_t$  being expressed in

VALUES OF  $E_t$  FOR THERMOMETERS OF JENA NORMAL-GLASS.

$t$	No. 245.			No. 246.			No. 247.		
	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.
$5^{\circ}$	+48	+48	0	+75	+75	0	+57	+57	0
10	44	45	-1	73	71	+2	55	54	+1
15	42	42	0	65	68	-3	53	51	+2
20	39	40	-1	64	64	0	51	49	+2
25	36	37	-1	60	60	0	51	46	+5
30	35	34	+1	58	57	+1	46	43	+3
35	34	31	+3	53	53	0	43	40	+3
40	21	28	-7	48	50	-2	38	37	+1
45	18	25	-7	46	46	0	32	34	-2
50	17	22	-5	43	42	+1	34	31	+3
55	15	20	-5	38	39	-1	26	29	-3
61	17	16	+1	33	34	-1	24	25	-1
65	11	14	-3	26	31	-5	18	23	-5
72.5	10	10	0	22	26	-4	18	19	-1
78	1	6	-5	19	22	-3	10	15	-5
82	7	4	+3	16	19	-3	13	13	0
91.5	2	-1	+3	11	12	-1	11	8	+3
96	0	-4	+4	7	9	-2	8	5	+3
100	-6	-6	0	6	6	0	3	3	0

thousandths of a degree. [To find the depression  $E_0 - E_t$  from these tables,  $E_0$  may be taken as  $E_5 + \cdot 003$  nearly. The values of  $E_0$  are not stated in Böttcher's paper.]

VALUES OF  $E_t$  FOR THERMOMETERS OF THURINGIAN AND  
ENGLISH GLASS.

$t$	No. 50. Thuring.			No. 20. Thuring.			No. 1115. English.		
	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.
5°	+526	+526	0	+246	+246	0	-110	-110	0
10	523	523	0	243	245	-2	125	112	-13
15	521	520	+1	240	244	-4	130	115	-13
20	517	515	+2	239	243	-4	135	120	-15
25	514	508	+6	240	240	0	135	126	-9
30	507	500	+7	236	238	-2	145	133	-12
35	501	491	+10	236	235	+1	150	142	-8
40	490	480	+10	229	231	-2	150	152	+2
45	473	468	+5	227	225	+2	158	163	+5
50	459	454	+5	223	220	+3	170	176	+6
55	428	439	-11	215	216	-1	195	190	-5
61	427	419	+8	216	209	+7	210	209	-1
65	407	404	+3	210	203	+7	213	222	+9
72·5	386	375	+11	200	193	+7	243	246	+3
78	361	351	+10	199	184	+15	240	271	+31
82	352	332	+20	188	177	+11	265	288	+23
91·5	313	285	+28	179	160	+19	278	332	+54
96	292	261	+31	169	151	+18	335	354	+19
100	238	238	0	143	143	0	375	375	0

The values headed "Calculated" in the first table are obtained by assuming that the differences in the zero reading  $E_t$  are proportional to the differences of  $t$ , and by identifying  $D$  with  $E_5 - E_{100}$ . These assumptions give

$$E_t = E_5 - \frac{D}{95}(t-5) = E_{100} + \frac{D}{95}(100-t). \quad \dots\dots(1), (2)$$

As the errors of observation may amount to  $0^{\circ}005$ , the agreement between calculation and observation is satisfactory; hence we infer that linear interpolation is permissible in dealing with the depressions of thermometers of Jena normal-glass—a great convenience in practice.

For the three thermometers to which the second table refers, the difference of  $E_t$  for an increase of  $5^\circ$  in  $t$  is much larger at high than at low temperatures, so that the linear law is not applicable. Böttcher applied to them Pernet's assumption<sup>1</sup> (for temperatures between  $0^\circ$  and  $100^\circ$ ) that  $E_0 - E_t$  is proportional to the square of  $t$ . Putting  $D_0$  for  $E_0 - E_{100}$ , this gives

$$E_t = E_0 - D_0 \left( \frac{t}{100} \right)^2, \dots\dots\dots (3)$$

which leads to a value of  $D$  or  $E_5 - E_{100}$  differing by only  $\frac{1}{4}$  per cent. from  $D_0$ ; so that we may write

$$E_t = E_0 - D \left( \frac{t}{100} \right)^2. \dots\dots\dots (4)$$

It is by (3) or (4) that the "calculated" values in the second table have been obtained.

The greatest error of an observation in the case of the two thermometers 50 and 20 may be estimated at  $0^\circ\cdot005$ ; in the case of thermometer 1115, which was only divided to half degrees, it may be taken at  $0^\circ\cdot020$ . Comparing these errors with the three columns of differences, we may say that the calculation is fairly satisfactory from  $0^\circ$  to  $70^\circ$ .

**Other Formulae for Depression.** Employing the more general formula<sup>2</sup>

$$E_t = E_{100} + a(100 - t) + b(100 - t)^2 \dots\dots\dots (6)$$

Böttcher finds, for the three thermometers 245, 246, 247,

$$a = \cdot00055, \quad b = \cdot000\ 0008$$

The formula gives

$$E_0 - E_t = (a + 200b)t - bt^2,$$

which reduces to Pernet's assumption (4) when  $a + 200b$  is negligible, the value of  $D_0$  being then  $D_0 = -100^2b$ . It would seem that these conditions are nearly fulfilled, between  $0^\circ$  and  $70^\circ$ , by Thuringian thermometer glass and English and French lead glass.

For Tonnelot's thermometers of *verre dur*, Guillaume has found<sup>3</sup> the depression-formula

$$E_0 - E_t = \cdot0008886t + \cdot000\ 001084t^2,$$

<sup>1</sup> Carl's *Repertorium*, 11. 294 (1875).

<sup>2</sup> Winkelmann, *Handb.*, II. 2. 29.

<sup>3</sup> *Travaux et mémoires du Bureau international des poids et mesures*, tom. V.

which, by the smallness of the coefficient of  $t^2$  compared with that of  $t$ , shows that linear interpolation is applicable.

The value of the depression-constant  $D_0$  or  $E_0 - E_{100}$  comes out .0997, which is sensibly .10, and practically the same as that of the Thuringian glass thermometer No. 20. This shows that the magnitude of the depression-constant is not of itself a sufficient index of the goodness of a thermometer glass.

**Depressions after Long Continuance in Ice Bath.** In order that a thermometer may show its true maximum of depressibility, it must be sufficiently old. It must also have been for so long a time in the ice bath before warming, that the effects of previous warming have been effaced. Observations in which these conditions appear to have been fulfilled, were made by Thiesen, Scheel, and Sell,<sup>1</sup> upon thermometers of Jena normal-glass and of Tonnelot's *verre dur* (four of each), and afterwards upon thermometers of normal-glass and of the borosilicate 59<sup>III</sup> (three of each). All the instruments had been for several weeks in the ice bath, and were then kept for a considerable time at each of the temperatures 25°, 50°, 75°, 100°. The results were summed up in the three following formulae:

$$\text{Normal-glass 16}^{\text{III}}: E_0 - E = .06484 \frac{t}{100} + .03104 \left( \frac{t}{100} \right)^2.$$

$$\text{Borosilicate 59}^{\text{III}}: E_0 - E_t = .04936 \frac{t}{100} - .01456 \left( \frac{t}{100} \right)^2.$$

$$\text{Verre dur: } E_0 - E_t = .10036 \frac{t}{100} + .00928 \left( \frac{t}{100} \right)^2.$$

A second calculation was made, from which the less certain observations were omitted. It gave

$$\text{Normal-glass: } E_0 - E_t = .0748 \frac{t}{100} + .0236 \left( \frac{t}{100} \right)^2.$$

$$\text{Verre dur: } E_0 - E_t = .1199 \frac{t}{100} - .0052 \left( \frac{t}{100} \right)^2.$$

The following tables for 16<sup>III</sup> and 59<sup>III</sup> were calculated by Scheel<sup>2</sup> from the first two formulae:

<sup>1</sup> *Zeitschr. f. Instrum.*, 16. 58 (1896).

<sup>2</sup> *Ibid.*, 17; *Beiblatt*, No. 13, 98 (1897).



DEPRESSION OF THERMOMETER OF  $16^{\text{III}}$  IN THOUSANDTHS  
OF A DEGREE.

Deg.	0	1	2	3	4	5	6	7	8	9
0	0	1	1	2	3	3	4	5	5	6
10	7	8	8	9	10	10	11	12	13	13
20	14	15	16	17	17	18	19	20	21	21
30	22	23	24	25	26	27	27	28	29	30
40	31	32	33	34	35	35	36	37	38	39
50	40	41	42	43	44	45	46	47	48	49
60	50	51	52	53	54	55	56	57	58	60
70	61	62	63	64	65	66	67	68	69	71
80	72	73	74	75	76	78	79	80	81	82
90	83	85	86	87	88	90	91	92	93	95
100	96									

DEPRESSION OF THERMOMETER OF  $59^{\text{III}}$  IN THOUSANDTHS  
OF A DEGREE.

Deg.	0	1	2	3	4	5	6	7	8	9
0	0	0	1	1	2	2	3	3	4	4
10	5	5	6	6	7	7	8	8	8	9
20	9	10	10	11	11	11	12	12	13	13
30	14	14	14	15	15	15	16	16	17	17
40	17	18	18	19	19	19	20	20	20	21
50	21	21	22	22	22	23	23	23	24	24
60	24	25	25	25	26	26	26	27	27	27
70	27	28	28	28	29	29	29	29	30	30
80	30	30	31	31	31	31	32	32	32	32
90	33	33	33	33	34	34	34	34	34	35
100	35									

Collecting together the results for each glass, and using the notation

$$E_0 - E_t = pt + qt^2,$$

we have the following list of values:

NORMAL-GLASS $16^{\text{III}}$ .		$p \times 10^5$	$q \times 10^5$	$D$
Böttcher,	- - - - -	71	- 0.08	0.063
Thiesen, Scheel,	} 1st formula,	64.84	0.3104	0.096
and Sell,		74.8	0.236	0.098

BOROSILICATE GLASS 59 <sup>III</sup> .			
	$p \times 10^5$	$q \times 10^5$	$D$
Thiesen, Scheel, and Sell,	49.36	- 0.1456	0.035
VERRE DUR.			
Guillaume, - - - - -	88.86	0.1084	0.100
Thiesen, Scheel, ) 1st formula, 100.36		0.0928	0.110
and Sell, ) 2nd formula, 119.9		- 0.052	0.115

The values given under the heading  $D$  are obtained by putting  $t=100$  in the formulae. For the normal-glass 16<sup>III</sup> they are considerably larger than the original determinations mentioned in Art. 111.

**114. Coefficients of After-working.** Let  $v_0$  be the original volume of a piece of glass at  $0^\circ$ ; and when it has been maintained for some time at  $t^\circ$ , and is then again brought to  $0^\circ$ , let its volume be

$$v_0 + v' = v_0(1 + A't + B't^2);$$

then the ratio of the additional volume  $v'$  to the original volume  $v_0$  is the measure of the afterworking. This ratio is

$$\frac{v'}{v_0} = A't + B't^2.$$

To show how this is related to the depression of zero of a thermometer produced by raising the thermometer to  $t^\circ$ ; let  $\beta$  be the mean coefficient of cubic expansion of the glass of the thermometer between  $0^\circ$  and  $100^\circ$ ,

$\gamma$  the mean coefficient of expansion of mercury from  $0^\circ$  to  $100^\circ$ ,

$v_0$  the volume of the mercury at  $0^\circ$ ,

$g$  the original volume of a degree at  $0^\circ$ .

Then the volume of the mercury at  $100^\circ$  is  $v_0(1 + 100\gamma)$  and is equal to  $(v_0 + 100g)(1 + 100\beta)$ ; whence we find rigorously

$$g = \frac{v_0(\gamma - \beta)}{1 + 100\beta}, \dots\dots\dots(1)$$

or approximately

$$g = v_0(\gamma - \beta).$$

When the thermometer, after being raised from its original temperature  $0^\circ$  to  $t^\circ$ , is restored to the ice bath, the volume left

vacant between the mercury and the original zero-mark will be

$$v' = v_0(A't + B't^2),$$

and the depression  $d$  will be  $v'/g$ , that is,

$$d = \frac{A't + B't^2}{\gamma - \beta} \dots\dots\dots(2)$$

If the observed values of depression are expressed by  $d = pt + qt^2$ , we have

$$A' = (\gamma - \beta)p \quad . \quad B' = (\gamma - \beta)q \dots\dots\dots(3)$$

Taking Thiesen's values of  $p$  and  $q$  for the three thermometer glasses, as given in last article, with the values of  $\beta$  derived from the results given in Art. 99 (for the mercury thermometer scale), and  $\gamma = \cdot 000182$ , we find for  $A'$  and  $B'$ :

	$A' \times 10^8$	$B' \times 10^8$
Normal-glass 16 <sup>III</sup>	10.2	·049
Borosilicate 59 <sup>III</sup>	8.1	—·024
<i>Verre dur</i>	15.9	·015

It is of interest to compare the mean coefficient of afterworking between  $0^\circ$  and  $t^\circ$ , which is  $A' + B't$  (and which we denote by  $\sigma$ ), with the mean coefficient of cubical expansion from  $0^\circ$  to  $t^\circ$  (which we denote by  $\beta$ ). The numbers are

	$10^8 \sigma$	$10^8 \beta$	$100 \frac{\sigma}{\beta}$
Normal-glass 16 <sup>III</sup>	15.1	2424.7	·6228
Borosilicate 59 <sup>III</sup>	5.7	1779.2	·3204
<i>Verre dur</i>	17.4	2334.3	·7454

All the above are from Thiesen and Scheel's determinations. Böttcher's mode of experiment was more in conformity with the ordinary use of thermometers. His data for normal thermometer glass 16<sup>III</sup>, with  $\beta = 24 \times 10^{-6}$ , and  $\gamma$  as above, lead to

$$A' = 11.2 \times 10^{-8} \quad . \quad B' = -\cdot 013 \times 10^{-8}.$$

**115. Depression of Boiling-point Thermometers.** Boiling-point thermometers afford an easy means of determining the barometric pressure to within a quarter of a millimetre; they are therefore well suited for the measurement of altitudes in exploring expeditions. That their use for this purpose is appreciated, may

be inferred from Wiebe's statement that 29 boiling-point thermometers were made at the Reichsanstalt during the first eleven months of its existence.

A necessary condition of their trustworthiness is the permanency of their zero points after successive heatings to the same temperature. This can only be secured by the use of suitable glass in their construction. From researches described by Wiebe, in a report of proceedings at the Reichsanstalt,<sup>1</sup> it appears that, unless this precaution is attended to, their indications are uncertain to the extent of  $0^{\circ}\cdot 1$ , equivalent to more than three millimetres of pressure.

The investigation was suggested in the following way. Two thermometers, numbered 42 and 43, of Thuringian glass, when compared with a standard on Sept. 7, 1888, at temperature  $87^{\circ}$ , were found to require the corrections

$$-0^{\circ}\cdot 05, \qquad -0^{\circ}\cdot 24.$$

They were then kept for 15 minutes at  $100^{\circ}$ , and their zeros were found to be thereby lowered by the amounts

$$0^{\circ}\cdot 43, \qquad 0^{\circ}\cdot 45.$$

Being left till Sept. 10 at the temperature of the room ( $15^{\circ}$  to  $20^{\circ}$ ) and then again compared at  $87^{\circ}$ , their corrections were found to be

$$+0^{\circ}\cdot 08, \qquad -0^{\circ}\cdot 09,$$

showing depressions  $0^{\circ}\cdot 13$ ,  $0^{\circ}\cdot 15$  as compared with the observations of Sept. 7.

This change attracted Wiebe's attention; and he followed it up by elaborate tests of two thermometers, No. 125 of Jena glass, and No. 31 of Thuringian glass.

The thermometers were first compared several times in alcohol vapour at  $78^{\circ}\cdot 5$ ; they were then kept for half an hour at the boiling point of water, and then again compared repeatedly at  $78^{\circ}\cdot 5$ ; several comparisons at  $0^{\circ}$  being made between these various observations. The results are given in the two following tables, the first containing the observations at  $0^{\circ}$ , and the second those at the higher temperatures. Each result is the mean of four separate readings made with a small telescope.

<sup>1</sup> *Zeitschr. f. Instrum.*, 8. 362 (1888).



The first table shows that the thermometers were exposed to the temperature  $78^{\circ}\cdot 5$  during four successive periods, together amounting to 134 minutes, the total depressions thus produced

1888	Determination of Zero.	No. 125.	No. 31.
September 17.	After rest at $15^{\circ}$	+ $0^{\circ}\cdot 071$	+ $0^{\circ}\cdot 128$
"	" 7 min. at $78^{\circ}\cdot 5$	$\cdot 038$	- $0\cdot 189$
"	" 7 " $78^{\circ}\cdot 5$	$\cdot 035$	$\cdot 207$
"	" 64 " $78^{\circ}\cdot 5$	$\cdot 033$	$\cdot 310$
"	" 56 " $78^{\circ}\cdot 5$	$\cdot 031$	$\cdot 337$
"	" 32 " $100^{\circ}\cdot 2$	$\cdot 018$	$\cdot 510$
"	" 22 " $78^{\circ}\cdot 5$	$\cdot 028$	$\cdot 411$
September 18.	" rest at $13^{\circ}$	$\cdot 060$	$\cdot 267$
"	" 48 min. at $87^{\circ}\cdot 7$	—	$\cdot 383$

being  $\cdot 040$  and  $\cdot 465$ . The first of these heatings lasted 7 minutes, and produced depressions  $\cdot 033$  and  $\cdot 317$ . The further heating for periods amounting to 127 mins. produced

1888.	Time.	No. 125.	No. 31.	1888.	Time.	No. 125.	No. 31.
Sept. 17.	11 h. 33 m.	In alcohol vapour.		Sept. 17.	1 h. 34 m.	$78^{\circ}\cdot 492$	$78^{\circ}\cdot 491$
"	36	$78^{\circ}\cdot 466$	$78^{\circ}\cdot 648$	"	36	$\cdot 491$	$\cdot 491$
"	39	$\cdot 483$	$\cdot 646$	"		Changing to $79^{\circ}\cdot 5$	
"	52	In alcohol vapour.		"	59	$\cdot 489^{\circ}$	$\cdot 460^{\circ}$
"	58	$\cdot 493^{\circ}$	$\cdot 592^{\circ}$	"	2 h. 4 m.	$\cdot 492$	$\cdot 466$
"	12 h. 9 m.	In alcohol vapour.		"	9	$\cdot 492$	$\cdot 466$
"	15	$\cdot 486^{\circ}$	$\cdot 571^{\circ}$	"	11	$\cdot 494$	$\cdot 460$
"	21	$\cdot 492$	$\cdot 571$	"		Comparison at $100^{\circ}\cdot 2$	
"	23	$\cdot 491$	$\cdot 562$	"	3 h. 26 m.	In alcohol vapour.	
"	26	$\cdot 495$	$\cdot 546$	"	33	$\cdot 469^{\circ}$	$\cdot 334^{\circ}$
"	32	$\cdot 495$	$\cdot 539$	"	35	$\cdot 481$	$\cdot 347$
"	33	$\cdot 492$	$\cdot 546$	"	39	$\cdot 484$	$\cdot 356$
"	36	$\cdot 496$	$\cdot 538$	"	40	$\cdot 486$	$\cdot 369$
"	38	$\cdot 492$	$\cdot 534$	"	44	$\cdot 488$	$\cdot 374$
"	43	$\cdot 493$	$\cdot 533$	"	47	$\cdot 487$	$\cdot 385$
"	49	$\cdot 493$	$\cdot 530$				
"	54	$\cdot 492$	$\cdot 521$	Sept. 18.	12 h. 59 m.	In alcohol vapour.	
"	56	$\cdot 493$	$\cdot 520$	"	1 h. 6 m.	$78^{\circ}\cdot 703$	$78^{\circ}\cdot 476$
"	1 h. 1 m.	$\cdot 493$	$\cdot 516$	"	12	$\cdot 706$	$\cdot 500$
"	4	$\cdot 495$	$\cdot 509$	"	43	$\cdot 704$	$\cdot 506$
"	19	In alcohol vapour.		"	47	$\cdot 704$	$\cdot 519$

further depressions  $\cdot 007$  and  $\cdot 148$ . The further exposure to the temperature of boiling water for 32 mins. made the total depressions amount to  $\cdot 053$  and  $\cdot 638$ .

The second table throws further light on the behaviour of the two thermometers.

After the comparison at 1h. 36m., Sept. 17, the temperature of the vapour rose to  $79\cdot 5$ , owing to an increase in the pressure; and the observations were not resumed till the pressure had again become normal. The barometer remained nearly constant on Sept. 17, and was 3 mm. higher on Sept. 18.

If we leave out of account the early observations taken before the instruments had quite attained the temperature of the bath, the readings of the Jena thermometer are all in good agreement, even including those taken after exposure to the temperature of boiling water. On the other hand, the thermometer of Thuringian glass shows a continually increasing depression during the whole time of its exposure even to the alcohol vapour. The depression comes into evidence even at the beginning; the thermometer reading lower although its temperature was really rising. Before exposure to the temperature of boiling water, the depression had attained the value  $0^{\circ}\cdot 19$ , and after this exposure it was about  $0^{\circ}\cdot 30$ . Wiebe calls attention to this circumstance as showing that the use of Thuringian glass for boiling-point thermometers is out of the question.

Since the introduction of boiling-point thermometers of Jena normal-glass, it has been frequently pointed out<sup>1</sup> that these instruments are fully competent to take the place of barometers, even in travels of great extent; and the same may be said *a fortiori* of thermometers of the borosilicate glass 59<sup>III</sup>. In the case of this latter, the depression of zero resulting from such heatings as are required in the use of the instrument, would be quite immaterial. Moreover the instruments would be much less perishable than mercurial barometers, being able to bear jolts, as well as sudden changes of temperature. If made of glass that has been skilfully cooled, and subjected to artificial ageing, there will be no necessity to test them at  $0^{\circ}$ , and several centimetres can thus be saved in their length.

#### 116. Secular Rise in Unused Thermometers. Some

<sup>1</sup> See Grützmacher, *Zeitschr. f. Instrum.*, 17. 200 (1897).

information on the secular rise of zero in thermometers of Jena normal-glass is given by the observations of F. Allihn published in the *Zeitschrift für Analyt. Chemie*, 28, 435, and 29, 381 (1889-1890), which are reproduced in the following table. The twelve instruments on which they were made were by Warmbrunn, Quilitz and Co., and were divided to tenths of a degree.

No.	Freezing-Points Observed.				Total Rise.
	Shortly after Making.		Feb., 1889.	Mar., 1890.	
106	March, 1886	0°·00	+ 0°·03	+ 0°·04	0°·04
108	" "	+ 0°·01	·02	·04	·03
665	August, 1886	·01	·03	·05	·04
667	" "	·02	·04	·05	·03
668	" "	·02	·05	·06	·04
669	" "	·03	·06	—	—
670	September, 1886	·00	·03	·04	·04
671	August, 1886	·05	·09	·09	·04
672	" "	·05	·08	·08	·03
673	" "	·03	·07	—	—
850	February, 1888	·00	·03	—	—
853	May, 1888	·00	·04	—	—

The first set of readings were taken a few weeks after the making of the instruments, which then remained unused till Feb. 1889, when their zeros were again tested; and in March 1890 those of them which still remained unused were again tested. The total rise, in about 4 years, varies from 0°·03 to 0°·04.

**117. Effects of Higher Temperatures.** The creeping up of zero with long exposure to high temperatures has been a frequent subject of investigation for the last fifty years or more. We shall deal only with researches which include comparisons of Jena-glass thermometers with other thermometers.<sup>1</sup>

<sup>1</sup> The papers cited as Wiebe I., Wiebe II., Allihn, Schott, are the following:

- I. H. F. Wiebe. On changes of mercurial thermometers at high temperatures. *Zeitsch. f. Instrum.*, 8. 373 (1888).
- II. H. F. Wiebe. On the employment of mercurial thermometers at high temperatures. *Zeitsch. f. Inst.*, 10. 207 (1890).
- III. F. Allihn. On rise of zero in mercurial thermometers of Jena normal-glass. *Zeitsch. f. Analytische Chemie*, 28. 435 (1890).
- IV. O. Schott. Study of some physical properties of glasses, and on a valuable new glass for thermometry. *Zeitschr. f. Instrum.*, 11. 330 (1891).

The older observations showed that, when a thermometer is maintained for a long time at a high constant temperature, its zero rises, first quickly, and then more and more slowly, tending probably to a limit dependent on the temperature; further, that the thermometer is thereby rendered less susceptible to change of zero at more moderate temperatures.

Wiebe brought together (I. 374) the observations of Person, Kopp, and Crafts, and confirmed and extended them by his own. Allihn's researches are in good agreement with Wiebe's. Schott's paper includes the recently produced borosilicate glass, and also describes researches calculated to throw light on the causes of rise of zero when thermometers are heated.

#### Amount and Progress of Rise of Zero for Various Glasses.

Wiebe published (I. 375) a short account of his experiments, performed in the years 1877-1881, on thermometers all of which were of Thuringian glass. One of his results may here be quoted. Two thermometers about 9 months old, were exposed to temperatures which increased by steps up to  $300^{\circ}$ , each exposure lasting a few minutes, and being succeeded by immersion in the ice bath. In this experiment, the depression increased with each step up to  $250^{\circ}$ ; but when the two thermometers were raised to  $300^{\circ}$  for five minutes, their depressions, which had gradually advanced to  $0^{\circ}5$  and  $0^{\circ}6$ , were diminished by  $0^{\circ}1$ . Extended experiments on the temperatures at which such reversals occur seem never to have been made.

Wiebe also made a series of comparative observations on the elevations of zero for thermometer glasses of different compositions.

Date.	Aggregate Exposure.	Position of Zero.					
		18 <sup>III</sup>	14 <sup>III</sup>	16 <sup>III</sup>	20 <sup>III</sup>	Eng. Glass.	17 <sup>III</sup>
1885—November 11.	3½ hours	0°·14	0°·30	0°·29	0°·34	0°·38	0°·60
„ „ 13.	6½ „	0°·31	0°·61	0°·63	0°·57	1°·04	1°·57
„ „ 14.	10¼ „	0°·66	0°·94	1°·07	1°·88	2°·33	3°·07
„ „ 19.	13¼ „	0°·80	1°·09	1°·24	—	2°·73	3°·60
„ „ 20.	19¼ „	1°·11	1°·40	1°·57	—	3°·63	—
Mean ratio to 18 <sup>III</sup> ,	- - -	1°·0	1°·6	1°·7	2°·4	3°·2	4°·8

Thermometers of the Jena glasses 14<sup>III</sup>, 16<sup>III</sup>, 17<sup>III</sup>, 18<sup>III</sup>, 20<sup>III</sup>, as well as of English crystal (see Art. 111), all of them several



months' old, and up to that time only exposed to moderate temperatures, were simultaneously raised several times to the temperature  $300^{\circ}$ , for periods of a few hours' duration. The positions of their zeros after each heating are exhibited in the foregoing table.<sup>1</sup> For the sake of clearer comparison, Wiebe computed, for each period of exposure, the ratios of the readings to the reading of  $18^{\text{III}}$ , and then took the means, which are given at the foot of the table.

The following are the results of some comparisons which he made<sup>2</sup> between the Jena normal-glass  $16^{\text{III}}$  and Thuringian glass. The values for  $16^{\text{III}}$  are the means of the results given by two new thermometers in July 1888. The values for Thuringian glass are derived, with the aid of interpolation, from observations also made on new thermometers. The temperatures were in all cases between  $360^{\circ}$  and  $370^{\circ}$ . The elevations of zero were more than three times as great for the Thuringian as for the Jena glass.

Duration of Heating.	Elevation of Zero.		Ratio.
	$16^{\text{III}}$	Thuringian.	
8 hours	$1^{\circ}51$	$4^{\circ}62$	1 : 3·1
13 „	1·89	6·56	1 : 3·5
16 „	2·21	7·30	1 : 3·3

Wiebe concludes with a detailed account of the behaviour of three thermometers, which have been mentioned in Art. 111 under the designations  $F_1$ ,  $F_3$ ,  $F_4$ .  $F_1$  was of the German potash glass used in the middle of the nineteenth century for the construction of thermometers;  $F_3$  and  $F_4$  were of Thuringian glass. According to Wiebe's table, the elevations of zero produced were :

$F_1$	after 38 hours at $260^{\circ}$	$= 0^{\circ}73$ ,
$F_3$	„ 32 „ „	$= 1^{\circ}37$ ,
$F_4$	„ 38 „ „	$= 2^{\circ}15$ .

Allihn, in his researches, heated the thermometers in a sand-bath, in order to avoid the chemical attack of the hot water on the glass, which might possibly occur in the usual liquid bath. The arrangements were such that the temperature could be kept

<sup>1</sup> Wiebe, I. 377.

<sup>2</sup> *Ibid.*, 378.

in the neighbourhood of  $300^{\circ}$ , with fluctuations not exceeding  $10^{\circ}$ . The mean temperature is taken by Allihn as  $290^{\circ}$ . Three thermometers were selected for the tests; two of them by Warmbrunn, Quilitz and Co., of Jena normal-glass, and one of Thuringian glass. The two former were unused thermometers, about a week old, with nitrogen above the mercury, divided to whole<sup>1</sup> degrees from  $0^{\circ}$  to  $360^{\circ}$ . The third (also unused), was about five weeks old, and was similarly divided, but without nitrogen. The observations of zero were in most cases made 24 hours subsequent to the exposures to high temperature. The results are contained in the following table. Before the commencement of the first heating, all three instruments read  $0^{\circ}0$  in the ice-bath.

Duration of Exposure.	Position of Zero.		
	Jena Normal-Glass.		Thuringian.
5 hours	+1°0	+1°0	+2°1
5 „	1°3	1°5	2°7
5 „	1°5	1°7	3°1
5 „	1°6	1°8	3°4
5 „	1°7	1°9	3°6
5 „	1°8	2°0	3°7
25 „	2°0	2°2	4°2

In Wiebe's researches above-mentioned, a thermometer of 16<sup>III</sup> showed a rise of zero  $1^{\circ}57$ , after  $19\frac{1}{4}$  hours continuous exposure to  $300^{\circ}$ . Allihn here finds, after four exposures of five hours each, a rise  $1^{\circ}6$  to  $1^{\circ}8$ ; the agreement is therefore pretty close. All through Allihn's observations, the Thuringian glass shows nearly double the elevation of the Jena normal-glass.

Wiebe afterwards extended his researches to higher temperatures, up to  $500^{\circ}$ .<sup>2</sup> Mercurial thermometers are generally used only up to  $300^{\circ}$ , because at higher temperatures the mercury (in vacuum thermometers) begins to boil. Boiling can be prevented by filling the space above the mercury with nitrogen or some other gas indifferent to mercury.<sup>3</sup>

<sup>1</sup>[Dr. Hovestadt suggests in a footnote that this may be a misprint for tenths of a degree.]

<sup>2</sup> Wiebe, II.

<sup>3</sup> Carbonic acid is now commonly employed.

If the gas is introduced at atmospheric pressure at  $20^\circ$ , and there is a space equal to  $r$  degrees above the  $n^{\text{th}}$  degree of the scale, then, when the mercury stands at  $n$  degrees, the volume of the gas has been reduced from  $r+n-20$  to  $r$ , so that even if its temperature were not raised, its pressure would be  $1 + \frac{n-20}{r}$  atmospheres.

Wiebe used five thermometers of Jena normal-glass, numbered 279, 281, 282, 283, 284. They were "Einschluss" thermometers,<sup>1</sup> with an enlargement at the top of the capillary tube, and were filled with nitrogen intended to prevent boiling at  $450^\circ$ .

If we put  $n=450$ , and equate  $1 + \frac{n-20}{r}$  to  $4\frac{1}{2}$ , which is the pressure (in atmospheres) of mercurial vapour at  $450^\circ$ , we get  $r=123$  as the volume of nitrogen required.

The scale of No. 281 reached down to  $0^\circ$ ; those of the other four began a little below  $100^\circ$ .

The investigation was begun by exposing the two thermometers numbered 281 and 282, for successive intervals of a few minutes, to temperatures rising by successive steps up to  $475^\circ$ ; and the following results were obtained:

	No. 281. Position of freezing.	No. 282. Position of boiling.
Before heating -	$0^\circ \cdot 0$	$100^\circ \cdot 0$
After 5 min. at $100^\circ$ -	$0 \cdot 0$	—
„ 5 „ 200 -	$0 \cdot 0$	—
„ 5 „ 300 -	$-0 \cdot 1$	—
„ 5 „ 400 -	$+0 \cdot 9$	$100 \cdot 5$
„ 5 „ 450 -	—	$103 \cdot 2$
„ 15 „ 475 -	$+9 \cdot 0$	$109 \cdot 5$

In explanation of these results, it is to be noted that No. 281 had on the previous day been heated to  $211^\circ$ —an operation which

<sup>1</sup> The *Einschluss thermometer* [enclosure-thermometer] has its stem enclosed within an outer glass tube sealed on to the stem at both ends, leaving the bulb exposed. The divisions are not on the stem, but on a thin glass plate held close to the stem by glass seals attached to the outer tube. The pattern is common in Germany, but is not made in England. The ordinary pattern is called, for distinction, *Stabthermometer* [rod thermometer].—J. D. E.

had already depressed its zero. It accordingly showed no change till heated above this temperature. Its first change is a further depression of  $0^{\circ}1$  by heating to  $300^{\circ}$ . The depression is changed to an elevation by heating to  $400^{\circ}$ . In Thuringian glass (as stated on p. 262), Wiebe found a similar change from depression to elevation, not at  $400^{\circ}$  but at  $300^{\circ}$ .

By further heating at  $420^{\circ}$  and  $460^{\circ}$ , further elevations of freezing point and boiling point were produced, but at a slower rate, as the following record shows:

Successive Exposures.	No. 281. Position of freezing.	No. 282. Position of boiling.
1 hour at $420^{\circ}$	$11^{\circ}1$	$112^{\circ}0$
$\frac{3}{4}$ „ 460	15.8	116.2
$1\frac{1}{4}$ „ 460	19.9	120.2
$1\frac{1}{4}$ „ 420	20.3	120.8
$1\frac{3}{4}$ „ 420	20.7	121.1

The other three thermometers were subjected to the same treatment as these two, and showed finally the boiling points:

No. 279.	No. 283.	No. 284.
$122^{\circ}0$	$123^{\circ}2$	$120^{\circ}4$

These three instruments were then subjected for four hours to a temperature of about  $500^{\circ}$  in fused lead chloride. This produced a considerable lowering of the boiling points, which persisted after subsequent heating at  $450^{\circ}$ , and must therefore be regarded as indicating yielding of the glass bulb to the strong internal pressure when softened by heat. The depressed boiling points were

$101^{\circ}0$	$104^{\circ}6$	$106^{\circ}2$
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In preliminary tests, Wiebe subjected two thermometers of the borosilicate 59<sup>III</sup> to the temperature  $300^{\circ}$  for 30 hours.<sup>1</sup> One was treated in the ordinary way; and the bulb of the other, before filling with mercury, had undergone the "fine-cooling" process. The zero of the first was raised  $3^{\circ}9$ ; that of the second only  $0^{\circ}1$  or  $0^{\circ}2$ .

<sup>1</sup>Schott, 334.



Schott himself undertook further experiments with this glass.<sup>1</sup> The thermometers which he tested had at the upper end of the tube a bulb about as large as that at the lower end, so that rise of the mercury in the tube could not much affect the pressure of the gas above it. This gas was nitrogen at an initial pressure of 10 atmospheres. Two of the thermometers were kept from two to three days without intermission at from  $470^{\circ}$  to  $477^{\circ}$ , then for nine days in a thermoregulator at  $360^{\circ}$ , and then cooled down to ordinary temperature. The mercury finally stood from  $13^{\circ}$  to  $15^{\circ}$  too high. The pressure of the gas must have reached between 27 and 28 atmospheres.

Finally Schott heated a thermometer of this kind up to the softening point of the glass. The temperature was measured by a Jolly's gas-thermometer, the gas being hydrogen, and the glass 59<sup>III</sup>. The gas-thermometer and the thermometer to be tested were heated together in a jacketed sheet-iron cylinder, from which only the enlargement at the end and a small portion of the tube of the mercurial thermometer projected. The heating was continued until, in spite of the gradual elevation of temperature which was going on, the mercurial column in the gas thermometer began to fall, indicating softening of the glass. The temperature attained was estimated at  $667^{\circ}$ , after making allowance for the distension of the softened bulb under the internal pressure. Without this allowance the calculation gave  $596^{\circ}$ .

Hence it appears that for a period of half an hour a temperature averaging  $640^{\circ}$  was maintained. The bulb of the mercurial thermometer must therefore have withstood an internal pressure of from 10 to 15 atmospheres. Its capacity had increased about 10 per cent.

We may mention finally some tests applied by Grützmacher<sup>2</sup> to two high-temperature thermometers of the glass 122<sup>III</sup>, which is a baryta borosilicate free from alkali. The instruments were maintained at temperatures lying between  $300^{\circ}$  and  $350^{\circ}$ , with the following results:

After 18 hours,	-	-	elevation	$0^{\circ}21$
„ 44 „	-	-	„	$0^{\circ}41$
„ 60 „	-	-	„	$0^{\circ}51$

<sup>1</sup> Schott, 332.

<sup>2</sup> *Zeitschr. f. Instrum.*, 15. 262 (1895).

These are even better than the results obtained with the borosilicate 59<sup>III</sup>.

**Permanence of Raised Zero.** One of the six thermometers which Wiebe tested for five days, in November, 1885,<sup>1</sup> by 19¼ hours' aggregate exposure to the temperature 300°, was of Jena normal-glass 16<sup>III</sup>. On this instrument some subsequent observations were made.<sup>2</sup> On Nov. 10, before the experiments already quoted, its zero reading was 0°·11. On Nov. 24, when they were just completed, it was 1°·68—a rise of 1°·57, as stated in the table already given.

The thermometer was left to itself till Feb. 23, 1886, and its zero reading was then found to be 1°·73. After another rest of nearly 1½ years, its reading was 1°·75. It was then subjected to several long-continued heatings at 260°, with the following results, which show a small increase to a definite limit practically attained in the last observation.

1888, July 14, after 4½ hours at 260°, reading	1°·80
18, " 5 " "	1°·83
19, " 4 " "	1°·85
Sept. 4, " 4 " "	1°·86

It is thus seen that 19 hours of heating at 300° prevent the production of any considerable further rise under subsequent exposure to 260°. "For chemical thermometers of Jena normal-glass, a 24-hour heating at 300° before graduation will suffice, in most cases, to ensure that any elevations of zero in subsequent use shall be inconsiderable."

Further experiments on the constancy of the raised zero were made<sup>3</sup> at still higher temperatures with the three thermometers numbered 279, 283, 284 already mentioned.<sup>4</sup>

The softening of the glass at 500° had left the boiling-points at the positions 101·0, 104·6, 106·2, as already stated. Subsequent heatings between 400° and 450° were found to produce rise of boiling-point readings, but on a much smaller scale than before heating at 500°. After a time, heating at 400° or 450° produced no further change of boiling-point reading.<sup>5</sup> The

<sup>1</sup> See page 262.

<sup>2</sup> Wiebe, I. 377.

<sup>3</sup> Wiebe, II. 209.

<sup>4</sup> See page 265.

<sup>5</sup> A mixture of equal parts of potassic and sodic nitrates, fused in an enamelled vessel, was the heating medium employed.

observations are given in the following table, which commences with the heating at 500°, already mentioned:

Date.		Boiling-Point Readings.		
		No. 279.	No. 283.	No. 284.
July 12	After 4 hours at 500°	101°·0	104°·6	106°·2
„ 15	„ 9 „ 450	103°·2	105°·9	108°·1
„ 20	„ 18 „ 450	104°·4	106°·7	108°·9
„ 22	„ 5 „ 450	104°·4	106°·6	109°·1
„ 23	„ 4 „ 400	104°·5	—	109°·1
„ 25	„ 12 „ 420	104°·4	—	109°·0
Sept. 4	„ 41 days' rest	104°·4	—	108°·9
„ 6	„ 8 hours at 450	104°·4	—	109°·1

From these results, Wiebe concludes that mercury thermometers of Jena normal-glass, with nitrogen above the mercury, can be used with confidence for measuring temperatures up to 450°, if they have been previously fortified by long-continued heating.

Thermometers of the borosilicate glass 59<sup>III</sup> can be used for still higher temperatures, as its temperature of softening is higher.

Schott states,<sup>1</sup> on Czapski's authority, that Baudin of Paris seasons his high-temperature thermometers by keeping them for eight days in boiling sulphur, which has a temperature of about 445°.

Instead of heating and cooling without special precautions, Schott recommends that, before filling with mercury, the thermometer bulb should be subjected to the "fine-cooling" process, the benefit of which has been clearly proved<sup>2</sup> in the case of a thermometer of 59<sup>III</sup>.

When thermometers, after elevation of zero by heating, are left to themselves, they sometimes show further elevation, sometimes depression, and sometimes constancy. The normal-glass thermometer first mentioned in this section showed, after three months' rest, a rise of 0·05; No. 279, after 41 days' rest, showed no change; while No. 284, after the same rest, showed a depression of 0·1.

Winkelmann, in his experiments on the variation of elasticity

<sup>1</sup> Schott, 335.

<sup>2</sup> See page 266.

with temperature,<sup>1</sup> used two high-temperature thermometers of borosilicate glass, numbered 4142 and 4144, which showed the following changes of zero.<sup>2</sup>

				Position of Zero.	
				No. 4142.	No. 4144.
1893, August 18,	-	-	-	0·3	1·2
1895, May 16,	-	-	-	3·6	—
„ Dec. 20,	-	-	-	4·6	5·0
1896, Oct. 22,	-	-	-	4·0	4·4

In the interval from Dec. 20, 1895 (or, rather, from Jan. 24, 1896, when the heating ceased) to Oct. 22, 1896, the elevations of both thermometers were diminished by 0·6.

**Rise of Zero Compared with Depression-constant.** From his observed values of the elevations of zero produced in six thermometers of different glasses by continued heating, Wiebe deduces (as above stated)<sup>3</sup> “mean ratios,” which he adopts as representing the relative susceptibilities of the six glasses to this influence. They are reproduced in the subjoined table, under the heading *A*; and the depression-constants (as defined in Art. 109) for the same glasses are given under the heading *D*. It will be seen that the order of arrangement is the same for both.<sup>4</sup>

				<i>A</i>	<i>D</i>
18 <sup>III</sup>	-	-	-	1·0	0·04
14 <sup>III</sup>	-	-	-	1·6	0·06
16 <sup>III</sup>	-	-	-	1·7	0·06
20 <sup>III</sup>	-	-	-	2·4	0·20
English crystal	-	-	-	3·2	0·27
17 <sup>III</sup>	-	-	-	4·8	1·05

The following table<sup>5</sup> shows that the same rule holds for the three thermometers  $F_1$ ,  $F_3$ ,  $F_4$ , which have been previously mentioned:<sup>6</sup>

		Elevation.	<i>D</i>
$F_1$	After 38 hours at 260°	0°·73	0°·15
$F_3$	„ 32 „ 260	1·37	0·38
$F_4$	„ 38 „ 260	2·15	0·65

<sup>1</sup> See page 161.

<sup>2</sup> *Ann. d. Phys. u. Chem.*, 61. 141 (1897).

<sup>3</sup> See page 262.

<sup>4</sup> Wiebe, I. 377.

<sup>5</sup> *Ibid.*, 378.

<sup>6</sup> See page 263.



**Temporary Diminution of Depressibility.** These three thermometers ( $F_1$  being of old German potash glass, and  $F_3$ ,  $F_4$  of Thuringian glass) were subjected by Wiebe, between March 21, 1881, and Sept. 24, 1888, to numerous heatings at  $260^\circ$ , and numerous determinations of zero. The following extract from the record of these observations<sup>1</sup> contains the history of the thermometer  $F_4$  from March 21, 1881, to Aug. 31, 1888. In May, 1883, all three thermometers were opened, and, after cutting off a sample of the capillary tube for chemical analysis, heated till the mercury boiled, and sealed up again.

Date.		Zero-Point.	<i>D</i>
1881—March 21.	After several months' rest,	+0°·21	
„ „	„ half-an-hour at $100^\circ$ ,	-0°·44	0·65
1883—May.	Opened, boiled, resealed, -		
„ Sept. 19.	After two months' rest, -	+5°·22	
„ „	„ half-an-hour at $100^\circ$ ,	+4°·66	0·56
1884—Feb. 26.	„ 5 months' rest, -	+5°·34	
„ „	„ half-an-hour at $100^\circ$ ,	+4°·74	0·60
„ „ 27.	6½ hours at $250^\circ$ , - - -		
„ „ 29.	After 2 days' rest, - - -	+6°·29	
1885—July 21.	„ 17 months' rest, - -	+6°·61	
„ „ 22.	„ half-an-hour at $100^\circ$ ,	+6°·00	0·61
1888—July 13.	After 3 years' rest, - - -	+6°·74	
„ „	„ half-an-hour at $100^\circ$ ,	+6°·08	0·66
„ „	3 hours at $260^\circ$ , - - -		
„ „ 14.	3 hours at $260^\circ$ , - - -		
„ „ 17.	After 3 days' rest, - - -	+6°·58	
„ „ 17-20.	23 hours at $260^\circ$ , - - -		
„ „ 21.	After 1 day's rest, - - -	+7°·13	
„ Aug. 31.	„ 1 month's rest, - -	+7°·49	
„ „	„ half-an-hour at $100^\circ$ ,	+7°·07	0·42

The last column gives the depression-constant as observed after each half-hour of heating at  $100^\circ$ . The influence of previous heating on the depression-constant is here distinctly perceptible. On Sept. 19, 1883, shortly after the boiling and resealing, and again on Aug. 31, 1888, shortly after long heating at  $260^\circ$ , the depression-constant is considerably diminished. The other two

<sup>1</sup> Wiebe, I. 379.

thermometers  $F_1$  and  $F_3$  behaved in the same way. "One sees, from these results, that observations of depression, taken soon after the making of a thermometer, furnish a very dubious criterion of the suitability of the glass for thermometric use, inasmuch as the high temperatures employed in the making cause these depressions to be too small. To determine the full amount of after-effect characteristic of any glass, the thermometer must either be kept for many months or be artificially seasoned."

**Rise of Zero as a Consequence of Relief of Stress.** Schott has suggested that the rise of zero of a thermometer, produced by continued exposure to a high temperature, may be due to the removal of stress previously existing in the glass of the bulb. In his account of his observations on the diminution of double refraction by continued heating, in the case of strongly stressed glass cylinders,<sup>1</sup> he remarks that the gradual disappearance of the stresses which are present in all specimens of glass not cooled with extreme care, "is accompanied by a diminution of volume (involving increase of density), and, in thermometers, by diminished capacity of the bulb," which will of course produce advance of the mercurial column.<sup>2</sup> He goes on a little later to describe an arrangement which he employed for giving optical evidence of the existence of stress in the glass of a thermometer.<sup>3</sup>

A cylindrical thermometer is placed within a tall rectangular cistern, made of glass plates cemented together at the edges. When the vessel is filled with a transparent liquid having the same index as the glass of the thermometer, light passes through the tube without undergoing refraction, and the appearance presented is that of a vertical section through the axis of the thermometer. The usual test by polarised light (with crossed Nicols and a concave mirror) showed the characteristic bright and dark bands.

In strongly stressed cylinders of normal-glass, Schott observed, after heating to 400°-410°, a diminution of double refraction, indicative of diminished stress. With cylinders of borosilicate thermometer-glass, a similar diminution was found after heating to 430°-440°. Acting on the knowledge<sup>4</sup> that Baudin had employed boiling sulphur for the seasoning of high-temperature thermometers, he subjected the borosilicate glass 59<sup>III</sup> to a further

<sup>1</sup> See Art. 29.<sup>2</sup> Schott, 332.<sup>3</sup> *Ibid.*, 335.<sup>4</sup> See page 269.

test.<sup>1</sup> A short cylindrical piece of this glass with plane polished ends, which when first tested between two Nicols showed "more rings than could be counted," was kept in boiling sulphur for four days, and afterwards showed only three rings.

The diminution of stress shown by these optical tests is obtained without softening in the ordinary sense of the word. Thermometers of the glass 59<sup>III</sup> at temperatures between 470° and 477°, when subjected to internal pressures of 27 to 28 atmospheres, were not distended, but, on the contrary, had their zeros considerably raised,<sup>2</sup> and thermometers of 16<sup>III</sup> with nitrogen above the mercury also showed elevation of zero after heating at 475°.<sup>3</sup>

The possibility of producing, in strongly stressed glass cylinders, by exposure to even such a moderate temperature as 100°, and for a comparatively short time, permanent molecular displacements tending to relieve the stresses, is shown by Pulfrich's observations on cylinders of the silicate crown O. 662, which we have mentioned in page 218.

Taking these facts into account, and also the consideration that stress is more easily removed from the walls of a hollow vessel than from the substance of a solid cylinder, Schott's suggestion as to the cause of the rise of zero produced by heating mercury thermometers seems to be a satisfactory explanation of all the known facts.

In particular, these observations of Pulfrich's show that, after the displacement produced by maintenance at a given temperature has reached its limit, exposure to a higher temperature can make the displacement begin anew and rapidly advance. After a cylinder of O. 662 had remained immersed in boiling water for three hours, without distortion of its polished plane ends, five minutes' immersion in oil at 200° caused them to exhibit concavity. This is precisely analogous to the fact, established by all researches, that a thermometer whose zero has been raised by long-continued heating at a given temperature, until it has at length become stationary, will begin to exhibit further rise of zero when maintained at a higher temperature.

Indubitable proof that the rise of zero produced by maintaining a thermometer at 100°, is due to relief of stress existing in the

<sup>1</sup> Schott, 336.

<sup>2</sup> See page 267.

<sup>3</sup> See page 265.



bulb before filling with mercury, is furnished by Wiebe's experiment (mentioned on p. 249) in connection with artificial ageing. Two thermometers of borosilicate glass, one of which had been subjected to the "fine-cooling" process before filling, were both maintained for 12 hours at  $100^{\circ}$  and slowly cooled. Under this identical treatment, the fine-cooled thermometer had its zero raised only one-third as much as the other thermometer, which had not undergone special preparation.

The temperature of  $400^{\circ}$  at which, according to Schott's observations, the falling off of stress in cylinders of normal-glass is optically perceptible, shows itself as a critical temperature in experiments on change of zero. When Wiebe heated the thermometer No. 281 [p. 265] at successively higher temperatures up to  $475^{\circ}$ , for periods of a few minutes, depression was produced by heating at  $300^{\circ}$ ; but heating at  $400^{\circ}$  changed this into a much larger elevation. It has been already mentioned, in our account of these experiments, that a similar transition from depression to elevation occurred at  $300^{\circ}$  in the case of thermometers of Thuringian glass; the lower temperature of transition being a natural consequence of the lower melting point.

**Increase of the Fundamental Interval** [that is of the difference between the reading at the true temperature  $0^{\circ}$  and the reading at the true temperature  $100^{\circ}$ ]. The rise of zero produced by heating a thermometer is accompanied by increase of the fundamental interval. This fact was first detected by Crafts, and has been abundantly confirmed. It is attributed, by general consent, to diminution in the expansibility of the glass, and furnishes another argument in support of the view that the rise of zero is due to the relief of pre-existing stress; for we have seen, in Art. 98, that the expansibility of stressed glass may be greater by several per cent. than that of the same glass when freed from stress.

An observation by Wiebe on the thermometer No. 281 of Jena normal-glass will serve as an illustration. By continued strong heating, the zero point was finally raised to  $+20^{\circ}\cdot7$ , and the "fundamental interval" was at the same time changed from the initial value  $99^{\circ}\cdot9$  to the final value  $100^{\circ}\cdot4$ .

Let  $v_0$  be the volume of the mercury in the thermometer at  $0^{\circ}$ ,  $\gamma$  the mean coefficient of expansion of mercury between  $0^{\circ}$  and  $100^{\circ}$ ,  $\beta$  the mean coefficient of cubic expansion of the glass before



heating. Then the volume (at  $100^\circ$ ) of the space between the freezing and boiling points is  $100v_0(\gamma - \beta)$ .

Let  $\beta'$  be the diminished value of  $\beta$  after the heating. Then the volume between the new freezing and boiling points is  $100v_0(\gamma - \beta')$ . If  $n$  and  $n'$  are the values of the fundamental interval before and after the heating, we have<sup>1</sup>

$$\frac{n'}{n} = \frac{\gamma - \beta'}{\gamma - \beta}, \quad \text{or} \quad \frac{n' - n}{n} = \frac{\beta - \beta'}{\gamma - \beta}.$$

Putting  $n = 99.9$ ,  $n' = 100.4$ ,  $\gamma = 182 \times 10^{-6}$ , and  $\beta = 244 \times 10^{-7}$ , which is the observed value for Jena normal-glass cooled in the ordinary way (see Art. 98), we deduce  $\beta - \beta' = 7.9 \times 10^{-7}$ , showing a diminution of more than 3 per cent. in the expansibility of the glass.

**118. Comparison of Normal-glass Thermometers with one another and with other Mercurial Thermometers.** Wiebe compared, over the interval  $0^\circ$  to  $100^\circ$ , the indications of various mercurial thermometers, of Jena normal-glass and of other glasses.<sup>2</sup> Thiesen, Scheel, and Sell have since made comparisons, over the same interval, between normal-glass 16<sup>III</sup>, borosilicate glass 59<sup>III</sup>, and the *verre dur* used by Tonnelot.<sup>3</sup> For the interval  $100^\circ$  to  $300^\circ$ , Wiebe and Böttcher<sup>4</sup> have furnished data for comparison between several thermometers of 16<sup>III</sup>, in the course of their comparisons of mercury thermometers with the air thermometer.

**Comparisons between  $0^\circ$  and  $100^\circ$ .** Wiebe's comparisons were carried out at the Reichsanstalt in 1888 and 1889, on three normal-glass thermometers, numbered 245, 246, 247. The instruments were divided to tenths of a degree, and their errors of calibration were known. They had also been several times tested as regards their errors of "fundamental interval" for different positions of the zero point.

[<sup>1</sup>In this calculation, the volume between two given marks on the stem is treated as unchanged, in comparing initial and final states, at the same temperature. Its values at the boiling point are in fact as  $1 + 100\beta$  to  $1 + 100\beta'$ , and the ratio of these two is  $1 + 100(\beta - \beta')$  or  $1 + 8 \times 10^{-5}$ , which may be treated as unity.]

<sup>2</sup>*Zeitsch. f. Instrum.*, 10. 435 (1890).

<sup>3</sup>*Ibid.*, 15. 433 (1895).

<sup>4</sup>*Ibid.*, 10. 233 (1890).

Between  $5^{\circ}$  and  $55^{\circ}$  the comparisons were made in a water-bath, the whole of the mercurial column being always below the surface of the water. For higher temperatures up to  $96^{\circ}$ , the vapours of various liquids were used as immersing media, the boiling-point apparatus employed for the purpose being essentially a Rudberg boiling-tube with back-flow cooler.<sup>1</sup>

Four series of observations were made; the first in April 1888, on Nos. 246 and 247, from  $5^{\circ}$  to  $97^{\circ}$ ; the second in August 1888, on the same, from  $5^{\circ}$  to  $35^{\circ}$ ; the third in September 1888, on all three thermometers, from  $5^{\circ}$  to  $92^{\circ}$ ; and the fourth in April 1889, on all three, from  $5^{\circ}$  to  $96^{\circ}$ . Wiebe gives the results in four tables, one for each series.

In the first series, the difference between the reading of one thermometer and the mean of the two, averages  $0^{\circ}002$ , and amounts in only one instance to  $0^{\circ}005$ .

In the second, it averages  $0^{\circ}003$ , and once reaches  $0^{\circ}006$ .

The third series includes readings of all three thermometers at 17 temperatures of comparison. The average difference from the mean is  $0^{\circ}004$ , and the largest  $0^{\circ}009$ .

In the fourth series, which consists of readings of all three instruments at 16 temperatures, the average difference from the mean is  $0^{\circ}005$ ; the difference being, in three instances, greater than  $0^{\circ}01$ , and amounting in one instance to  $0^{\circ}019$ .

The differences did not follow any well-defined law. The outcome of the observations is, that thermometers of Jena normal-glass, after being corrected for errors of calibration, of zero, and of value of a degree, show complete agreement within the limit  $\pm 0^{\circ}01$ .

Wiebe further compared, between  $0^{\circ}$  and  $100^{\circ}$ , the above-mentioned three thermometers with a thermometer, No. 20, of Thuringian glass, another, No. 115, of English crystal, and a Tonnelot thermometer, No. 246.

The Thuringian thermometer, which was 70 years old, and had the relatively small depression-constant  $0^{\circ}14$ , gave, at temperatures below  $82^{\circ}$ , higher readings than the normal-glass thermometers, the difference amounting, at two points, to  $0^{\circ}05$ .

The English thermometer read lower than the Jena glass thermometers, the difference often amounting to  $0^{\circ}17$ .

<sup>1</sup> It is figured and minutely described in *Zeitsch. f. Instrum.*, 10. 27 (1890).

The Tonnelot thermometer was difficult to compare, as it had not the usual strip of white enamel. It was only tested up to  $30^\circ$ , and so far it agreed perfectly with the corrected reading of No. 246; that is to say, the differences noted never exceeded the possible errors of observation.

The observations of Thiesen, Scheel and Sell were (like those of Wiebe), conducted at the Reichsanstalt. The instruments, after the most exact determination of their errors (of calibration, zero point, and distance between fixed points), were compared in several series of observations. In some series the thermometers were in the usual upright position, in others they were horizontal. All the comparisons were made in a water-bath, the higher temperatures being maintained by a worm traversed by steam.

Three series of observations (the thermometers being vertical in one of them, and horizontal in the other two,) agreed in showing a systematic difference between normal-glass and *verre dur* thermometers, three instruments of each kind being observed.

Let  $t_{16}$  denote the mean reading of the three thermometers of the normal-glass 16<sup>III</sup>;  $t_T$  the mean reading of the three Tonnelot thermometers of *verre dur*; and  $t$  without suffix the mean  $\frac{1}{2}(t_{16} + t_T)$ .

Then, assuming that the difference between  $t_{16}$  and  $t_T$  is proportional to the product of the two intervals  $t - 0$  and  $100 - t$ , we have ( $x$  being a constant),

$$t_{16} - t = x \frac{t(100 - t)}{100^2},$$

$$t_T - t = -x \frac{t(100 - t)}{100^2}.$$

The value of  $x$  deduced from the observations was 0.0259.

Again, the mean reading of three thermometers of the borosilicate glass 59<sup>III</sup> being denoted by  $t_{59}$ , it was found that the observations agreed with the equation

$$t_{59} - t = -y \frac{t(100 - t)}{100^2},$$

the value of  $y$  being 0.3336.

By means of these formulae, the following table of differences between the three kinds of thermometers was calculated:

UNIT 0°·0001.

Temperature.	$t_{16} - t$	$t_{59} - t$	$t_T - t$	$t_{16} - t_{59}$	$t_T - t_{16}$	$t_T - t_{59}$
5° and 95°	+12	-158	-12	+171	- 25	+146
10 „ 90	23	300	23	323	47	277
15 „ 85	33	425	33	458	66	392
20 „ 80	41	534	41	575	83	492
25 „ 75	49	626	49	674	97	577
30 „ 70	54	701	54	755	109	646
35 „ 65	59	759	59	818	118	700
40 „ 60	62	801	62	863	124	738
45 „ 55	64	826	64	890	128	761
50°	65	834	65	899	129	769

The temperatures in the first column may be taken indifferently as  $t_{16}$ ,  $t_T$ , or  $t_{59}$ .

The comparisons between 100° and 300°, which we have now to describe, were carried out by Wiebe and Böttcher during May-September 1889, with seven normal-glass thermometers, numbered 253, 254, 255, 257, 258, 259, 271, which were made for the Reichsanstalt in Nov. 1887. All of them had enlargements (in their capillary tubes) whose capacities were known multiples of the volume of a degree (on a plan employed by Pernet in 1879).

Nos. 254 and 255 were graduated up to 160°, in fifths of a degree, and had two enlargements, one between 0° and 50°, the other between 50° and 100°.

Nos. 253 and 257 were graduated up to about 220°, in fifths of a degree, and had only one enlargement, which was between 0° and 100°.

Nos. 258, 259, and 271 were graduated up to about 350°, in half degrees, and had two enlargements, one between 0° and 100°, the other between 100° and 200°.

The calibration was effected by Pernet's apparatus, according to the method of Neumann and Thiesen. The correction for calibre in Nos. 253, 255, and 257 nowhere exceeded 0°·3. In the others it amounted, in some places, to more than a degree, but did not exceed half a degree at any point which entered into the measurements. Nos. 257 and 259, besides being calibrated soon after making, were recalibrated after they had been several times exposed to high temperatures. The second



calibration showed that the heating had made a difference, the lower portion of the tube having shrunk. In 257 the change amounted to  $0^{\circ}05$  at the point  $200^{\circ}$ , and in 259 to  $0^{\circ}04$  at the point  $300^{\circ}$ . The progress of the change was taken into account in the reductions. The calibration of the other thermometers was not carried out till they had been several times employed at high temperatures, and is not likely to have been much affected by their subsequent heatings. The interval between the two fixed points was checked several times in the case of each of the thermometers.

The correction for internal pressure amounted to  $0^{\circ}02$  or  $0^{\circ}03$  for Nos. 254, 255, 253, 257, and to  $0^{\circ}04$  for Nos. 258, 259, 279.

Each observation of temperature was immediately followed by an observation of freezing point.

The corrections for the non-immersed portions of the stems were determined with great care by means of small auxiliary thermometers, at proper heights, close beside the principal thermometers.

Corrections were fully applied for every known source of error.

The immersion-media were the vapours of 18 different liquids, having boiling-points spread over the interval from  $100^{\circ}$  to  $300^{\circ}$ . The first on the list was isobutylalcohol, boiling at  $105^{\circ}7$  at 760 mm., and the last diphenylamin, which at 751 mm. boils at  $301^{\circ}5$ . Two different forms of the already mentioned boiler with back-flow cooler were employed. One of them, of thin brass soft-soldered, was used up to  $160^{\circ}$ ; the other, of stout copper hard-soldered, for the higher temperatures.<sup>1</sup>

A complete list of the readings of the seven thermometers in these various vapours and the corrections applied is given by Wiebe and Böttcher in tabular form.<sup>2</sup> It brings out an unexpected closeness of agreement between the instruments. The difference of an individual thermometer from the mean of all in the same bath with it, usually amounts to only a few hundredths of a degree; its average is  $0^{\circ}022$ . Only once (in amylbenzoat vapour) did the difference of one thermometer from the mean reach  $0^{\circ}1$ .

<sup>1</sup>The exact details of all the arrangements here summarised are given in a paper devoted to the subject. *Zeitschr. f. Instrum.*, 10. 16 (1890).

<sup>2</sup>*Zeitschr. f. Instrum.*, 10. 238-243.

The following short extract will serve as a specimen of these results. It gives simultaneous corrected readings of the four thermometers 254, 255, 253, 257 in isobutylalcohol vapour ( $105^{\circ}\cdot7$ ); of the four thermometers 257, 258, 259, 271 in ethylbenzoat vapour ( $212^{\circ}\cdot2$ ); and of the three thermometers 258, 259, 271 in amylbenzoat vapour ( $259^{\circ}\cdot3$ ). The means of the simultaneous readings are given in the last column.

CORRECTED READINGS OF THE SEVEN THERMOMETERS.

254	255	253	257	258	259	271	Mean.
$105^{\circ}\cdot74$	$105^{\circ}\cdot73$	$105^{\circ}\cdot72$	$105^{\circ}\cdot71$	—	—	—	$105^{\circ}\cdot73$
$105^{\circ}\cdot74$	$105^{\circ}\cdot73$	$105^{\circ}\cdot71$	$105^{\circ}\cdot70$	—	—	—	$105^{\circ}\cdot72$
$105^{\circ}\cdot74$	$105^{\circ}\cdot73$	$105^{\circ}\cdot72$	$105^{\circ}\cdot71$	—	—	—	$105^{\circ}\cdot73$
			$212^{\circ}\cdot20$	$212^{\circ}\cdot24$	$212^{\circ}\cdot24$	$212^{\circ}\cdot25$	$212^{\circ}\cdot24$
			$212^{\circ}\cdot32$	$212^{\circ}\cdot33$	$212^{\circ}\cdot36$	$212^{\circ}\cdot35$	$212^{\circ}\cdot34$
			$212^{\circ}\cdot37$	$212^{\circ}\cdot38$	$212^{\circ}\cdot40$	$212^{\circ}\cdot38$	$212^{\circ}\cdot38$
			$212^{\circ}\cdot40$	$212^{\circ}\cdot43$	$212^{\circ}\cdot42$	$212^{\circ}\cdot44$	$212^{\circ}\cdot42$
				$259^{\circ}\cdot74$	$259^{\circ}\cdot65$	$259^{\circ}\cdot52$	$259^{\circ}\cdot64$
				$260^{\circ}\cdot23$	$260^{\circ}\cdot15$	$260^{\circ}\cdot12$	$260^{\circ}\cdot17$
				$260^{\circ}\cdot53$	$260^{\circ}\cdot41$	$260^{\circ}\cdot35$	$260^{\circ}\cdot43$
				$260^{\circ}\cdot62$	$260^{\circ}\cdot47$	$260^{\circ}\cdot49$	$260^{\circ}\cdot53$
				$260^{\circ}\cdot66$	$260^{\circ}\cdot53$	$260^{\circ}\cdot53$	$260^{\circ}\cdot57$

**119. Comparison with the Air Thermometer.** The above comparison of seven thermometers formed part of an elaborate investigation by Wiebe and Böttcher of the relation between temperature by mercurial thermometers and temperature by the air thermometer. The investigation included three series of researches. The first series (which were merely preliminary) were conducted in 1888; the second in January-March 1889; and the third in May-September of the same year.

Two different air thermometers were employed, one of them in the first, and the other in the second and third series. In both of them the temperature was measured by the pressure of air at nearly constant volume. For details of construction and reduction, we must refer to the original papers.<sup>1</sup>

The observations of the third series are given in full by Wiebe,<sup>2</sup> together with the following table of corrected results.

<sup>1</sup> *Zeitschr. f. Instrum.*, 10. 17 and 10. 233 (1890).

<sup>2</sup> *Ibid.*, 10. 238-243.

$T_q$  is corrected temperature by mercury thermometer, and  $T_l$  by air thermometer.<sup>1</sup> In each case, simultaneous readings of different mercury thermometers are not given separately, but are combined into a single mean.

DIFFERENCES BETWEEN NORMAL-GLASS THERMOMETER AND  
AIR THERMOMETER.

First Series.		Second Series.		Third Series.	
$T_q$	$T_l - T_q$	$T_q$	$T_l - T_q$	$T_q$	$T_l - T_q$
106°	+0°·01	—	—	105°·7	+0°·01
—	—	—	—	109·3	+0·03
—	—	113°·7	+0°·06	114·1	+0·04
—	—	—	—	124·6	+0·07
129	+0·09	127·6	+0·07	129·5	+0·09
138	+0·02	138·2	+0·07	139·1	+0·12
—	—	—	—	139·7	+0·11
—	—	148·3	0·00	148·6	+0·08
159	-0·15	158·7	-0·03	159·9	+0·11
184	+0·12	184·4	+0·07	184·1	+0·08
—	—	—	—	193·7	0·00
196	+0·04	—	—	199·4	+0·02
—	—	—	—	199·2	-0·05
211	-0·30	211·9	-0·39	212·3	-0·13
237	-0·99	236·6	-0·92	236·3	-0·48
—	—	261·0	-1·41	260·3	-0·95
—	—	289·5	-2·17	291·5	-1·64
—	—	303·9	-2·47	—	—

The three series agree fairly well with each other. There are, however, considerable discrepancies in the temperatures near 159°, which were observed in vapour of turpentine. In the first and second series, it was not found possible to make this vapour give a constant temperature; probably the liquid was not homogeneous. Above 200° the first and second series agree together, but differ by from 0°·2 to 0°·5 from the third. The formula

$$T_l - T_q = aT_q(100 - T_q) + bT_q(100 - T_q)^2$$

was selected for expressing the differences in terms of  $T_q$ ; and

<sup>1</sup>The subscript  $q$  stands for *Quecksilber* (quicksilver), and the subscript  $l$  for *Luft* (air).

the method of least squares, when applied to each series separately, gave the following values of  $a$  and  $b$ :

	$a$	$b$
First series, - -	$-210 \times 10^{-7}$	$-311 \times 10^{-9}$
Second series, - -	$-284 \times 10^{-7}$	$-370 \times 10^{-9}$
Third series, - -	$-280 \times 10^{-7}$	$-299 \times 10^{-9}$

The values of  $T_l - T_q$  calculated by employing these values of the coefficients  $a$  and  $b$  differ from the observed values by the following amounts (observed - calculated), expressed in hundredths of a degree:

First Series.	Second Series.	Third Series.
0	+ 2	- 1
+ 5	0	0
- 3	- 1	0
- 18	- 8	+ 1
+ 20	- 9	+ 2
+ 21	+ 11	+ 3
+ 2	- 8	+ 2
- 29	- 44	- 2
	- 11	+ 1
	+ 12	+ 4
	+ 45	0
		+ 5
		- 2
		0
		- 7
		- 12
		- 1

**Practical Conclusion.** In adopting a formula for practical use, Wiebe and Böttcher decided to rely upon the third series alone. It was the most complete; it gave the best agreement between calculation and observation; and it was the only series during which the zero point of the air thermometer remained steady. They accordingly adopted the values

$$a = -280 \times 10^{-7}, \quad b = -299 \times 10^{-9},$$

for the coefficients in the general formula already given. They have thus computed the following practical table,<sup>1</sup> for reducing

<sup>1</sup> *Zeitschr. f. Instrum.*, 10. 245.



the corrected readings of a thermometer of the Jena normal-glass  $16^{\text{III}}$  to the corresponding temperatures by air thermometer.

$T_q$	$T_l - T_q$	$T_q$	$T_l - T_q$	$T_q$	$T_l - T_q$
100°	0°·00	170°	+0°·08	240°	-0°·46
110	+0°·03	180	+0°·06	250	-0°·63
120	+0°·05	190	+0°·02	260	-0°·82
130	+0°·07	200	-0°·04	270	-1°·05
140	+0°·09	210	-0°·11	280	-1°·30
150	+0°·10	220	-0°·21	290	-1°·58
160	+0°·10	230	-0°·32	300	-1°·91

Finally, Wiebe computed, with these coefficients, the corrections  $T_l - T_q$  for normal-glass thermometers at temperatures below 100°, and compared them with the corrections found by Chappuis for reducing Tonnelot thermometers of *verre dur* to the nitrogen thermometer. In the following table, these two sets of corrections are given, in the columns headed "normal-glass" and "*Verre dur*."

$T_q$	Normal-Glass.	<i>Verre dur</i> .	Diff.	$t_T - t_{16}$
-20°	+0°·153	+0°·159	—	—
-10	+0°·067	+0°·067	—	—
0	0°·000	0°·000	0°·000	0°·000
+10	-0°·049	-0°·046	-0°·003	-0°·005
20	-0°·083	-0°·075	-0°·008	-0°·008
30	-0°·103	-0°·091	-0°·012	-0°·011
40	-0°·110	-0°·097	-0°·013	-0°·012
50	-0°·107	-0°·094	-0°·013	-0°·013
60	-0°·096	-0°·085	-0°·011	-0°·012
70	-0°·078	-0°·071	-0°·007	-0°·011
80	-0°·054	-0°·052	-0°·002	-0°·008
90	-0°·028	-0°·029	+0°·001	-0°·005
100	0°·000	0°·000	0°·000	-0°·000

The next column, headed "Diff." gives the excess of the normal-glass correction above the Tonnelot correction, which, if we identify the air thermometer with the nitrogen thermometer, should be the excess of the Tonnelot reading above the normal-glass reading, and should therefore agree with the values of  $t_T - t_{16}$  observed by Thiesen, Scheel and Sell, which are reproduced

in the last column (they were given to four decimals in Art. 118). The maximum discrepancy is  $0^{\circ}006$ .

**Application of Wiebe and Böttcher's Reductions to subsequent Observations.** In using vapour baths for the comparison of thermometers, if the boiling takes place at atmospheric pressure, the observer is restricted to particular temperatures, which may be very unevenly distributed over the range of the comparisons. Further complications are introduced, by the decomposition which many liquids undergo from contact with the hot walls of the boiler, and by the impurities which in many liquids can scarcely be avoided. Wiebe and Böttcher pointed out these difficulties, and remarked that, if suitable arrangements were employed for increasing and diminishing the pressure, so as to raise and lower the boiling points, a few liquids would suffice, and those which give trouble could be excluded.<sup>1</sup>

The plan thus indicated was afterwards carried out by W. Pomplun, at the Reichsanstalt.<sup>2</sup> His boiling point apparatus consisted essentially of a boiler, and an air-reservoir in connection with a closed manometer having a large air-bulb.

It was first used for comparisons of normal-glass thermometers above  $50^{\circ}$ , and proved very effective. The liquids employed were methyl-alcohol, distilled water, and amyl-acetate. The instruments compared were Nos. 244, 246, 253, 254, 270. The first was divided to fifths, and the second to tenths; the others have been described already. All were corrected in the usual way for calibre, distance between fixed points, zero, and internal pressure; and special attention was paid to the influence of external pressure. The corrected readings were then, by means of Wiebe and Böttcher's corrections, reduced to air-thermometer temperatures. The results showed very close consistency over the whole range of the comparisons,  $48^{\circ}$  to  $141^{\circ}$ .

**120. Mediate Reduction to Air Thermometer.** Grütz-macher<sup>3</sup> carried out comparisons of 15 thermometers of three other kinds of glass, with thermometers of Jena normal-glass 16<sup>III</sup>; and thus, by using Wiebe and Böttcher's reductions given above, compared his 15 thermometers with the air thermometer.

<sup>1</sup> *Zeitsch. f. Instrum.*, 10. 28 (1890).

<sup>2</sup> *Ibid.*, 11. 1 (1891).

<sup>3</sup> *Ibid.*, 15. 250 (1895). Communication from the Reichsanstalt.

Among them were six "inclosed thermometers" of borosilicate glass 59<sup>III</sup>. Two of these were divided to tenths from 0° to 100°; two others to fifths from 100° to 200°, with auxiliary graduation at 0°; and the remaining two to half-degrees from 200° to 300°, with auxiliary graduation at 0° and 100°. The divisions were in each case equidistant, and the calibre corrections were determined by the Neumann-Thiesen method. The distance between the fixed points was determined in the usual way; and also the coefficients for internal pressure, which, on account of the widenings, were required for the high-temperature thermometers.

Another group consisted of four thermometers, of the baryta borosilicate without alkali No. 122<sup>III</sup>. There had been insufficient experience in the manipulation of this glass, and the instruments were not so perfect in construction as could be desired for such an investigation. Two were divided to fifths from 0° to 100°. The other two were divided to half-degrees from 100° to 300°. Their corrections were determined in the same way as for the thermometers of 59<sup>III</sup>.

Lastly five thermometers of "Resistance-glass" by Greiner and Friedrichs of Stützerbach were tested, their graduations being to tenths from 0° to 100°. They were calibrated by a thread of mercury 50° long for the steps from 0° to 50° and from 50° to 100°; and also by a thread 10° long for each step of 10°. Only one of these thermometers was subjected to a complete calibration. The distance between its fixed points was determined in the usual way. Up to 50° the comparisons were made in the water bath; above this temperature, in the vapours of liquids boiling in the thermostat under ordinary atmospheric pressure.

Denoting by  $T_q$  the corrected mean reading of the thermometers of any one kind of glass—the corrections including zero-point, distance between fixed points, calibration, and, as far as necessary, internal pressure, and by  $T$  the temperature by air thermometer, deduced from the normal-glass thermometers by Wiebe and Böttcher's table, the formula

$$T - T_q = aT_q(100 - T_q) + bT_q(100 - q)^2$$

was assumed, and the values of  $a$  and  $b$  were then deduced from the observations by the method of least squares.

The following were the results :

		10 <sup>7</sup> <i>a</i> .	10 <sup>6</sup> <i>b</i> .
Glass 59 <sup>III</sup>	0° to 100°	+ 48·70	— 263·8
Glass 59 <sup>III</sup>	100° to 300°	— 72·33	— 425·9
Glass 122 <sup>III</sup>	0° to 100°	+ 93·48	— 82·45
Resistance glass	0° to 100°	— 316·9	— 373·76

For glass 59<sup>III</sup>, 0° to 100°, the calculated and observed values agree well, only 7 determinations out of 44 showing a difference exceeding 0°·01. The largest differences—going up to 0°·015 as a maximum—occurred where the boiling liquids had lost something of their purity. The “probable error” is 0°·003.

For the same glass from 100° to 300°, the probable error is 0°·09, even after the exclusion of the last three observations as uncertain. At the higher temperatures, the mercury was so near its boiling point (the space above it being nearly free of air) that the column was apt to break; and distillation of mercury, which frequently occurred at the end of the column, added to the uncertainty.

The coefficients *a* and *b* for the interval 0° to 100° can be used without much error between 100° and 200°; the values thus obtained agreeing within 0°·08 with those obtained by using the coefficients for 100° to 300°. Above 200° this approximate agreement does not continue; and at 300° the difference amounts to 1°·2. But the observations above 200° cannot be regarded as very accurate, and need confirmation.

For 122<sup>III</sup> between 0° and 100°, the calculated reduction to air thermometer has a probable error of 0°·005. The observations on this glass, like Wiebe's observations on English thermometer glass (Art. 112), indicate that, between 0° and 100°, the mercury thermometer reads lower than the air thermometer. The comparisons of the two high temperature thermometers of this glass showed considerable differences from the air thermometer; but these were due, at least in part, to defects in calibration and in evaluation of distance between fixed points.

For “resistance glass,” between 0° and 100°, the probable error is 0°·006. The largest difference from the air thermometer was found between 60° and 61° in chloroform vapour. Observations were not taken above 100°.

The tables given below have been calculated by using the four sets of values of *a* and *b* above given. They show that thermometers of the borosilicate 59<sup>III</sup> agree more closely with the air thermometer



than thermometers of normal-glass. They have also, as has been already stated, less liability to depression of zero by heating. The baryta borosilicate 122<sup>III</sup> surpasses even 59<sup>III</sup> in these respects.

$T_q$	$T - T_q$			$T_q$	$T - T_q$		
	59 <sup>III</sup>	122 <sup>III</sup>	Resist.-Gl.		59 <sup>III</sup>	122 <sup>III</sup>	Resist.-Gl.
0°	0°·000	0°·000	0°·000	50°	-0°·021	+0°·013	-0°·126
5	-0°·009	+0°·001	-0°·032	55	-0°·017	+0°·014	-0°·120
10	-0°·017	+0°·002	-0°·059	60	-0°·014	+0°·015	-0°·112
15	-0°·022	+0°·003	-0°·081	65	-0°·010	+0°·015	-0°·102
20	-0°·026	+0°·004	-0°·098	70	-0°·006	+0°·014	-0°·090
25	-0°·028	+0°·006	-0°·112	75	-0°·003	+0°·014	-0°·077
30	-0°·029	+0°·008	-0°·121	80	-0°·001	+0°·012	-0°·063
35	-0°·028	+0°·009	-0°·127	85	+0°·001	+0°·010	-0°·048
40	-0°·026	+0°·011	-0°·130	90	+0°·002	+0°·008	-0°·032
45	-0°·024	+0°·012	-0°·129	95	+0°·002	+0°·004	-0°·016
50	-0°·021	+0°·013	-0°·126	100	0°·000	0°·000	0°·000

FOR THERMOMETERS OF 59<sup>III</sup>.

$T_q$	$T - T_q$	$T_q$	$T - T_q$	$T_q$	$T - T_q$
100°	0°·00	135°	-0°·04	170°	-0°·27
105	0°·00	140	-0°·06	175	-0°·32
110	0°·00	145	-0°·08	180	-0°·39
115	0°·00	150	-0°·11	185	-0°·46
120	0°·00	155	-0°·14	190	-0°·53
125	-0°·01	160	-0°·18	195	-0°·62
130	-0°·02	165	-0°·22	200	-0°·71

Grützacher applies the following check to the correctness of his determinations. Let  $T_l - T_{16}$  denote the excess of the air thermometer over the normal-glass thermometer as determined by Wiebe and Böttcher;<sup>1</sup>  $T_{59} - T$  the excess of the borosilicate thermometer above the air thermometer according to Grützacher; and  $t_{16} - t_{59}$  the excess of normal-glass over borosilicate, as directly observed by Thiesen, Scheel, and Sell.<sup>2</sup> The sum of the three excesses is

$$(T_l - T) + (t_{16} - T_{16}) + (T_{59} - t_{59})$$

which ought to vanish, since each pair of bracketed terms is the

<sup>1</sup> See Art. 119.

<sup>2</sup> See Art. 118.

difference of two things which ought to be identical. Grützmacher has applied this test to the temperatures between  $0^{\circ}$  and  $100^{\circ}$ , and finds that the sum never exceeds  $0^{\circ}004$ .

H. Lemke<sup>1</sup> has since compared five other thermometers of  $59^{\text{III}}$  (through the medium of normal-glass thermometers) with the air thermometer, and represented the resulting corrections by a two-term formula, for the range  $100^{\circ}$  to  $200^{\circ}$ . His corrections differ on the average from Grützmacher's by not more than  $0^{\circ}02$ . The difference increases towards the top of the scale, becoming  $0^{\circ}03$  at  $195^{\circ}$ , and  $0^{\circ}04$  at  $200^{\circ}$ .

REDUCTION OF THERMOMETERS OF THE BOROSILICATE GLASS  
 $59^{\text{III}}$  TO THE AIR-THERMOMETER.

$T_q$	$T - T_q$	$T_q$	$T - T_q$	$T_q$	$T - T_q$	$T_q$	$T - T_q$
100°	0°00	125°	-0°03	150°	-0°13	175°	-0°33
101	0°00	126	-0°03	151	-0°13	176	-0°34
102	0°00	127	-0°03	152	-0°14	177	-0°35
103	0°00	128	-0°04	153	-0°15	178	-0°37
104	0°00	129	-0°04	154	-0°16	179	-0°38
105	0°00	130	-0°04	155	-0°16	180	-0°39
106	0°00	131	-0°04	156	-0°16	181	-0°40
107	0°00	132	-0°05	157	-0°17	182	-0°41
108	0°00	133	-0°05	158	-0°18	183	-0°43
109	0°00	134	-0°06	159	-0°19	184	-0°44
110	0°00	135	-0°06	160	-0°19	185	-0°45
111	0°00	136	-0°06	161	-0°20	186	-0°46
112	0°00	137	-0°07	162	-0°21	187	-0°48
113	-0°01	138	-0°07	163	-0°21	188	-0°49
114	-0°01	139	-0°08	164	-0°22	189	-0°51
115	-0°01	140	-0°08	165	-0°23	190	-0°52
116	-0°01	141	-0°08	166	-0°24	191	-0°53
117	-0°01	142	-0°09	167	-0°25	192	-0°55
118	-0°02	143	-0°09	168	-0°26	193	-0°56
119	-0°02	144	-0°10	169	-0°27	194	-0°57
120	-0°02	145	-0°10	170	-0°28	195	-0°59
121	-0°02	146	-0°11	171	-0°29	196	-0°60
122	-0°02	147	-0°11	172	-0°30	197	-0°62
123	-0°02	148	-0°12	173	-0°31	198	-0°64
124	-0°03	149	-0°12	174	-0°32	199	-0°66
125	-0°03	150	-0°13	175	-0°33	200	-0°67

<sup>1</sup> *Zeitschr. f. Instrum.*, 19. 33 (1899).

Finally, Lemke has deduced from his own observations considered jointly with Grützmacher's, having regard to their relative weights, the foregoing table of reductions for each degree from  $100^{\circ}$  to  $200^{\circ}$ .

**121. Relative Expansions of Liquid and Envelope.** In this article we suppose temperatures to be expressed in the scale of the air thermometer.

Let  $\gamma$  be the mean coefficient of expansion of mercury from  $0^{\circ}$  to  $t^{\circ}$ ;  $\beta$  the mean coefficient of expansion of the glass from  $0^{\circ}$  to  $t^{\circ}$ ;  $v_0$  the common volume at  $0^{\circ}$  of the mercury and of the interior space bounded by the zero mark, which we suppose to be correctly placed.

Then, at temperature  $t^{\circ}$ , this space has increased from  $v_0$  to  $v_0(1 + \beta t)$ , and the volume of the mercury has increased from  $v_0$  to  $v_0(1 + \gamma t)$ . The difference  $v_0(\gamma - \beta)t$  is the volume at  $t^{\circ}$  of the column of mercury which has passed the zero mark, and therefore of the portion of the tube between this mark and the mark which indicates  $t^{\circ}$  by air thermometer. Hence  $\frac{v_0(\gamma - \beta)t}{1 + \beta t}$  is the volume of the tube between these marks, measured at  $0^{\circ}$ ; and  $\frac{v_0(\gamma - \beta)t}{1 + \gamma t}$  is the volume that the mercury which has passed the zero mark would occupy, if reduced to  $0^{\circ}$ .

Thiesen<sup>1</sup> calls  $\frac{(\gamma - \beta)t}{1 + \beta t}$  the "expansion of the mercury relative to the glass" from  $0^{\circ}$  to  $t^{\circ}$ , and denotes it by  $\rho_t$ .

In like manner he calls the negative quantity  $\frac{(\beta - \gamma)t}{1 + \gamma t}$  the "expansion of the glass relative to the mercury" from  $0^{\circ}$  to  $t^{\circ}$ , and denotes it by  $\rho'_t$ . From the two equations

$$\rho_t = \frac{(\gamma - \beta)t}{1 + \beta t}, \quad \rho'_t = \frac{(\beta - \gamma)t}{1 + \gamma t}, \dots\dots\dots(1)$$

we have

$$1 + \rho_t = \frac{1 + \gamma t}{1 + \beta t}, \quad 1 + \rho'_t = \frac{1 + \beta t}{1 + \gamma t}, \dots\dots\dots(2)$$

<sup>1</sup> *Zeitschr. f. Instrum.*, 16. 50 (1896).

giving

$$\left. \begin{aligned} (1 + \rho_t)(1 + \rho'_t) &= 1, \\ \rho_t + \rho'_t + \rho_t \rho'_t &= 0, \end{aligned} \right\} \dots\dots\dots(3)$$

$$\rho_t = \frac{-\rho'_t}{1 + \rho'_t} \dots\dots\dots(4)$$

In an overflow thermometer which is just full at  $0^\circ$ ,  $-\rho'_t$  is the ratio of the overflow to the total quantity of mercury which filled the instrument at  $0^\circ$ .

**122. Thiesen's Experimental Results for Relative Expansion.** Overflow thermometers of small size are usually called *weight thermometers*. When very large, and constructed with a view to great accuracy, they are called *dilatometers*.

Thiesen, Scheel and Sell<sup>1</sup> made elaborate determinations of  $\rho'_t$  at the Reichsanstalt, with five dilatometers, two of which were of normal-glass 16<sup>III</sup>, two of Tonnelot's *verre dur*, and one of borosilicate glass 59<sup>III</sup>. The values headed  $-\rho'$  and  $\rho$  in the subjoined table were for  $t = 100$ . The dilatometer under examination was kept full of mercury at the temperatures  $0^\circ$  and  $100^\circ$

Dilatometer.	$-\rho'$	$\rho$	$100\gamma$
No. 1 of 16 <sup>III</sup>	0·01552494	0·01576976	0·0182327
No. 2 „	0·01550211	0·01574620	0·0182091
No. 1 of <i>verre dur</i>	0·01557575	0·01582220	0·0181934
No. 2 „	0·01557674	0·01582321	0·0181944
of 59 <sup>III</sup>	0·01618236	0·01644854	0·0182570

alternately, and the quantity of mercury which flowed alternately out and in was determined by weighing the small glass cup which received the overflow, the weight of mercury which filled the dilatometer at  $0^\circ$  being also known with sufficient exactness. The ratio of these two weights is  $-\rho'$ ; and  $\rho$  was deduced by the equation

$$\rho = \frac{-\rho'}{1 + \rho'}.$$

Different determinations with the same dilatometer agreed within

<sup>1</sup> *Zeitschr., f. Instrum.*, 16. 55 (1896).



one unit of the sixth decimal place; but the values of  $\rho'$  for the two dilatometers of 16<sup>III</sup> differ by 22 of these units. This must be ascribed to the fact that the two instruments were not made from portions of the same melting. The two dilatometers of *verre dur* were made from parts of one and the same glass tube, and they agree to one unit of the sixth place.

The values of  $100\gamma$ —that is the absolute expansion of mercury from  $0^\circ$  to  $100^\circ$ —given in the last column, were obtained by combining the values of  $\rho$  or of  $\rho'$  with the absolute expansions of the three glasses, as previously determined by Thiesen and Scheel (see Art. 99). We have, in fact, by putting  $t = 100$  in the first of equations (1),

$$100\gamma = 100\beta + \rho(1 + 100\beta) \dots \dots \dots (5)$$

The security for identity of the dilatometer glass with the glass of the tubes whose expansion was observed, was greater for No. 1 dilatometer of 16<sup>III</sup>, and for the dilatometer of 59<sup>III</sup>, than for the three others. Adopting the mean of these two, to five significant figures, we have

$$100\gamma = 0.018245.$$

This is in good agreement with Bosscha's and Wüllner's reductions of Regnault's observations.

As the internal volume of a thermometer tube between the marks  $0^\circ$  and  $100^\circ$ , measured at  $0^\circ$ , is  $v_0\rho$ , and the thermometer is graduated by dividing this volume into 100 equal parts; the volume from  $0^\circ$  to the mark  $T^\circ$ , measured at  $0^\circ$ , is  $v_0\rho\frac{T}{100}$ ; but it is also (by Art. 121)  $v_0\rho_t$ ; we have therefore

$$\rho_t = \frac{T}{100} \rho \dots \dots \dots (6)$$

In the investigation of Art. 121,  $t$  was the air thermometer temperature equivalent to  $T$ ; but the investigation and its result are equally applicable when  $t$  is the corresponding temperature by hydrogen thermometer. Hence if  $\rho$  (which stands for  $\rho_{100}$ , and is the same for all scales that have the two usual fixed points) is known for a particular glass, and also the differences between  $T$  for thermometers of this glass and  $t$  for the hydrogen scale, over a given range, equation (6) enables us to compute  $\rho_t$  over this range.

Chappuis' differences between Tonnelot thermometers and the hydrogen scale give, in combination with the above tabulated value of  $\rho$  for *verre dur*, the values of  $\rho_t$  for thermometers of *verre dur* between  $0^\circ$  and  $100^\circ$ . The comparisons<sup>1</sup> by Thiesen and Scheel of thermometers of  $16^{\text{III}}$  and  $59^{\text{III}}$  with Tonnelot thermometers, and so mediately with the hydrogen scale, give, with the above tabulated values of  $\rho$  for  $16^{\text{III}}$  and  $59^{\text{III}}$ , the values of  $\rho_t$  for thermometers of these two glasses over the same range. Again, since the definition of  $\rho_t$  is

$$\rho_t = \frac{(\gamma - \beta)t}{1 + \beta t},$$

where  $\gamma$  and  $\beta$  are the mean coefficients of expansion of volume of mercury and glass from  $0^\circ$  to  $t^\circ$ , the values of  $\rho_t$  for the three glasses, in conjunction with the values of  $\beta$  over the range  $0^\circ$  to  $100^\circ$ , which were previously found for these glasses by Thiesen and Scheel,<sup>2</sup> give for each glass a separate determination of  $\gamma$  over the range  $0^\circ$  to  $100^\circ$ . The calculation has been carried out by these authors,<sup>3</sup> and the resulting mean coefficient from  $0^\circ$  to  $t^\circ$  of the hydrogen scale is

$$\gamma_t = \cdot 000\,18161 + \cdot 000\,000\,0078t.$$

**Observations above  $100^\circ$ .** The relative expansion  $\rho_t$  of mercury for the borosilicate glass  $59^{\text{III}}$ , which is specially suited for high-temperature thermometers, was investigated by Mahlke at the Reichsanstalt, up to  $500^\circ$ , by means of dilatometers of this glass.<sup>4</sup> Five dilatometers were used, and each of them had a graduated neck, of sufficient length to include a range of  $100^\circ$ . The plan of procedure was, to introduce, in the first instance, such a quantity of mercury that the graduated portion included the range  $0^\circ$  to  $100^\circ$ ; then to expel so much mercury that the range was  $100^\circ$  to  $200^\circ$ ; then to expel more, so as to make it  $200^\circ$  to  $300^\circ$ , and so on. The arrangements for this purpose are fully described and figured in Mahlke's paper.

Three dilatometers on this plan were employed; they are designated I, II, and III. Each of them had its tube divided

<sup>1</sup> Page 277.

<sup>2</sup> See page 221.

<sup>3</sup> *Zeitschr. f. Instrum.*, 16, 58 (1896).

<sup>4</sup> *Ann. d. Phy. u. Chem.*, 53, 965 (1894). Extracts are given in *Zeitschr. f. Instrum.*, 15, 171 (1895).

into millimetres for a length of 20 cm. All three were maintained for three hours at a temperature between  $530^{\circ}$  and  $540^{\circ}$  before the mercury was introduced. The quantity introduced was such that, in the ice-bath, the end of the column stood at the zero of the divisions. The rest of the tube was exhausted of air to permit of calibration. When the calibration had been effected, the first measurement of distance between the two fixed points ( $0^{\circ}$  to  $100^{\circ}$ ) was made. Then, having regard to the temperatures to which they were to be exposed, the tube of I was filled up with carbonic acid at 16 atmospheres, and II and III with the same gas at 8 and 24 atmospheres.<sup>1</sup> A cooling arrangement was employed to keep the gas at its initial pressure in the observation of high temperatures.

When the distance between the two fixed points was remeasured after the filling with gas, it was found to have undergone no material change; whence it was inferred that the expansion of mercury from  $0^{\circ}$  to  $100^{\circ}$  is practically the same at 24 atmospheres as at 1 atmosphere.

The next operation was to separate a thread of mercury of such length that the boiling point should retreat from the end of the scale to its beginning. The instrument was then immersed in methyl-benzoate vapour, and the rise of the mercury to  $200^{\circ}$  was observed. Another separation of a thread of mercury brought the  $200^{\circ}$  point to the beginning of the scale, and an observation was made in a nitre bath at  $290^{\circ}$ . These intervals of approximately  $100^{\circ}$  to  $200^{\circ}$  and  $200^{\circ}$  to  $290^{\circ}$  were succeeded by the intervals  $290^{\circ}$  to  $350^{\circ}$ ,  $350^{\circ}$  to  $400^{\circ}$ ,  $400^{\circ}$  to  $450^{\circ}$ ,  $450^{\circ}$  to  $500^{\circ}$ . In each of the three last an intermediate point was also observed. No. II dilatometer was the only one that underwent all these operations without sustaining damage.

The exact temperatures were read off on mercury thermometers, and reduced to the air thermometer by a table of known corrections.

**Reduction of the Observations above  $100^{\circ}$ .** Let  $v_0$  be the volume at  $0^{\circ}$  of the original quantity of mercury, and  $e$  the volume at  $100^{\circ}$  of one of the equal parts into which the tube is divided by the millimetre scale. Also let  $n$  be the number of these

<sup>1</sup>At a later stage the pressure in I was changed to 8, and in II to 16 atmospheres. *Ann. l.c.*, 977.

parts between the two fixed points, and  $M$  the ratio defined by  $v_0 = Me$ . Then we have

$$100(\gamma - \beta)v_0 = ne,$$

giving

$$M = \frac{n}{100(\gamma - \beta)} \dots\dots\dots (7)$$

Let the first portion of mercury removed have at  $0^\circ$  the volume  $\mu e$ , leaving the remaining volume at  $0^\circ$ ,  $(M - \mu)e$ .

The dilatometer, with this mercury in it, is heated first to a temperature  $t_1$  near  $100^\circ$ , and then to a temperature  $t_2$  near  $200^\circ$ , temperatures being reckoned by air thermometer. Let  $e_1$  and  $e_2$  denote the volumes of a scale division at these temperatures. Then we have

$$n_1 e_1 = (M - \mu) e (\gamma_1 - \beta_1) t_1,$$

$$n_2 e_2 = (M - \mu) e (\gamma_2 - \beta_2) t_2,$$

$\gamma_1, \beta_1$  being the mean coefficients between  $0^\circ$  and  $t_1^\circ$ , and  $\gamma_2, \beta_2$  between  $0^\circ$  and  $t_2^\circ$ .

Dividing the first equation by  $e_1$ , the second by  $e_2$ , and using the values

$$e = e_0(1 + 100\beta),$$

$$e_1 = e_0(1 + \beta_1 t_1),$$

$$e_2 = e_0(1 + \beta_2 t_2),$$

we find  $n_2 - n_1 = (M - \mu)(1 + 100\beta)(\rho_2 - \rho_1), \dots\dots\dots (8)$

and from the directly observed magnitudes  $n_1, n_2$ , the difference  $\rho_2 - \rho_1$  can be computed.

As regards  $\mu$ , we have defined it by making  $\mu e$  denote the volume at  $0^\circ$  of the separated column, whose volume at  $100^\circ$  we will call  $me$ . This makes

$$\mu = \frac{m}{1 + 100\gamma} \dots\dots\dots (9)$$

If we modify the definition by making  $\mu e$  denote the volume at  $0^\circ$  of a separated column which at the temperature  $t_1$  (not differing much from  $100^\circ$ ) occupies  $m$  divisions, then, since the volume of this mercury at  $t_1$  is  $\frac{me(1 + \beta t_1)}{1 + 100\beta}$ , its volume at  $0^\circ$  is

$\frac{me(1 + \beta t_1)}{(1 + 100\beta)(1 + \gamma t_1)}$ , that is,  $\frac{me}{(1 + 100\beta)(1 + \rho_1)}$ , by equation (2) of Art. 121,  $\rho_1$  denoting the value of  $\rho_t$  for  $t = t_1$ . This gives

$$\mu = \frac{m}{(1 + 100\beta)(1 + \rho_1)} \dots\dots\dots (9a)$$



In like manner, from the observed number of divisions occupied by the column of mercury which is detached at the temperature  $t_2$ , we can calculate  $\rho_3 - \rho_2$ , and so proceed step by step.

In the numerical calculation, Mahlke employs the values

$$1 + 100\beta = 1.0017783,$$

$$1 + 100\gamma = 1.0182161,$$

the former being Thiesen and Scheel's determination for the glass in question, and the latter Broch's deduction from Regnault's observations. These give

$$\rho = .016409.$$

Mahlke deduces the following values of the expression  $(1 + 100\beta) \frac{\rho_k - \rho_i}{t_k - t_i}$  for the successive intervals  $t_k - t_i$ . (See equation (8)).

From $t_i$ to $t_k$ .		Values of the expression.
From	0° to 100°	0.00016438
„	99.43 „ 199.69	16493
„	201.43 „ 289.44	17044
„	288.39 „ 349.80	17698
„	353.9 „ 373.9	17691
„	373.9 „ 397.7	17936
„	353.9 „ 397.7	17820
„	396.7 „ 424.0	18318
„	424.0 „ 452.2	19114
„	396.7 „ 452.2	18735
„	456.0 „ 475.2	19304
„	475.2 „ 495.0	19358
„	456.0 „ 495.0	19217

As regards the first value,  $t_i$  is 0;  $t_k$  is 100;  $\rho_i$  is 0; and  $(1 + 100\beta) \frac{\rho_k}{t_k}$  is  $\gamma - \beta = .00016438$ .

To deduce a numerical formula for  $\rho_t$  in terms of  $t$ , assume, for temperatures between 0° and 290°,

$$(1 + 100\beta) \frac{d\rho_t}{dt} = a + bt + ct^2,$$

which gives

$$(1 + 100\beta) \frac{\rho_k - \rho_i}{t_k - t_i} = \frac{a(t_k - t_i) + \frac{1}{2}b(t_k^2 - t_i^2) + \frac{1}{3}c(t_k^3 - t_i^3)}{t_k - t_i}.$$

Substituting the observed values of the left-hand member, we have numerical equations in  $a$ ,  $b$ ,  $c$ , from which Mahlke deduces

$$10^6 a = 165.873, \quad 10^6 b = -0.478, \quad 10^6 c = 0.002669,$$

giving, for temperatures between  $0^\circ$  and  $290^\circ$ ,

$$10^6(1+100\beta)\rho_t = 165.873t - 0.239t^2 + 0.0008897t^3.$$

For temperatures between  $290^\circ$  and  $500^\circ$ , a four-term formula is assumed, and the result deduced by the method of least squares is,

$$\begin{aligned} (1+100\beta)\rho_t = & 0.32931 + 10^{-6} \times 161.544(t-200) \\ & + 10^{-8} \times 12.89(t-200)^2 \\ & + 10^{-10} \times 4.858(t-200)^3 \\ & + 10^{-12} \times 0.8489(t-200)^4. \end{aligned}$$

The following table of values of  $(1+100\beta)\rho_t$  and of  $\rho_t$  is computed by these two formulae:

$t$	$(1+100\beta)\rho_t$	$\rho_t$
100°	0.016437	0.016408
200	0.032931	0.032873
300	0.049974	0.049885
325	0.054397	0.054300
350	0.058853	0.058749
375	0.063342	0.063230
400	0.067868	0.067748
425	0.072446	0.072317
450	0.077098	0.076961
475	0.081857	0.081712
500	0.086754	0.086600

**Reduction of the Borosilicate Glass High-Temperature Thermometer to the Air Thermometer.** Equation (6), which may be written

$$\frac{T}{100} = \frac{\rho_t}{\rho_{100}}, \dots\dots\dots(6)$$

enables us to compute the borosilicate thermometer temperatures  $T$  which correspond to the air-temperatures  $t$  in the above table.

Mahlke deduces

$t$	$T$	$t$	$T$	$t$	$T$
0°	0°	325°	330°·9	425°	440°·7
100	100	350	358·1	450	469·1
200	200·4	375	385·4	475	498·0
300	304·1	400	412·3	500	527·8

This gives  $-0.4$  as the correction at  $200^\circ$  for reducing the borosilicate thermometer to the air thermometer. Grützmacher and Lemke (Art. 120), by direct comparison with the air thermometer, found  $-0.7$ . In view of this discrepancy, it is worth while to examine the separate results given for the interval  $t_1$  to  $t_2$  by the three dilatometers I, II, and III. As a preliminary step, we shall first deduce a convenient expression for  $T_2 - T_1$  in terms of the data of observation. We have, by (6);

$$T_2 - T_1 = \frac{100}{\rho} (\rho_2 - \rho_1).$$

But by (8),

$$\rho_2 - \rho_1 = \frac{n_2 - n_1}{(M - \mu)(1 + 100\beta)},$$

where

$$M = \frac{n}{100(\gamma - \beta)}; \quad \mu = \frac{m}{1 + 100\gamma} = \frac{-m\rho'}{100(\gamma - \beta)}.$$

Hence

$$\rho_2 - \rho_1 = \frac{n_2 - n_1}{1 + 100\beta} \frac{100(\gamma - \beta)}{n + m\rho'} = \rho \frac{n_2 - n_1}{n + m\rho'},$$

and

$$T_2 - T_1 = 100 \frac{n_2 - n_1}{n + m\rho'}, \dots\dots\dots (10)$$

$T_2$  was calculated by adding the value of this expression to  $T_1$ , which, from its closeness to the fixed point  $100^\circ$ , was readily determined with sufficient exactness. The following are the values of the elements in the formula for the three dilatometers:

	I.	II.	III.
$n_2 - n_1$	151·35	159·89	160·46
$n$	152·47	161·35	162·15
$m$	135·15	148·09	155·28

Mahlke adopts  $\gamma = \cdot 000\ 182\ 161$ ,  
 $\beta = \cdot 000\ 017\ 783$ ;

which give  $\rho' = -\cdot 016\ 144$ .

$T_1$  may be identified with  $t_1$ , their difference being certainly less than  $0\cdot 001$ . We thus obtain

	I.	II.	III.
$t_2$	199°·9	199°·6	199°·5
$T_2$	200·2	200·1	199·8
$T_2 - t_2$	0·3	0·5	0·3

The employment of Thiesen and Scheel's value of  $\rho'$  in place of Mahlke's will not make enough difference to alter any of the three differences 0·3, 0·5, 0·3, each of which is decidedly smaller than the value 0·7 found by Grützmacher and Lemke.

**123. Tables for Reducing Mercury Thermometers of 16<sup>III</sup>, 59<sup>III</sup>, and Verre Dur, to the Hydrogen Thermometer.** Let  $t_H$  denote temperature on the hydrogen scale,  $t_{16}$ ,  $t_{59}$ ,  $t_T$  temperatures on the scales of thermometers of 16<sup>III</sup>, of 59<sup>III</sup>, and of Tonnelot's *verre dur*.

Chappuis<sup>1</sup> adopts, for the reduction of the Tonnelot thermometer to the international hydrogen scale, the formula

$$10^{-3}(t_H - t_T) = -0\cdot 10921037(100 - t)t \\ + 5\cdot 8928597(100^2 - t^2)t10^{-4} \\ - 1\cdot 15773247(100^3 - t^3)t10^{-6}.$$

K. Scheel<sup>2</sup> gives, as an equivalent formula,

$$t_H - t_T = \frac{(100 - t)t}{100^2} (-0\cdot 61859 + 0\cdot 0047351t \\ - 0\cdot 000011577t^2), \dots\dots\dots(1)$$

and deduces similar formulae for the Jena glass thermometers. The comparisons carried out by Thiesen, Scheel and Sell (Art. 118) gave the formulae of reduction

$$t_T - t_{16} = -0\cdot 0518 \frac{(100 - t)t}{100^2}, \\ t_T - t_{59} = +0\cdot 3077 \frac{(100 - t)t}{100^2},$$

<sup>1</sup> *Trav. et mém. du bur. internat.*, 6. 116 (1888).

<sup>2</sup> *Ann. d. Phy. u. Chem.*, 58. 168 (1896).





VALUES OF  $t_{59} - t_H$  IN THOUSANDTHS OF A DEGREE.

	0	1	2	3	4	5	6	7	8	9
0°	0	3	6	9	11	14	16	18	20	22
10	24	25	27	28	30	31	32	33	34	35
20	35	36	36	37	37	37	38	38	38	38
30	38	37	37	37	37	36	36	35	35	34
40	34	33	32	32	31	30	29	28	27	27
50	26	25	24	23	22	21	20	19	18	17
60	16	15	14	14	13	12	11	10	9	8
70	8	7	6	5	5	4	3	3	2	1
80	1	0	0	0	-1	-1	-1	-1	-2	-2
90	-2	-2	-2	-2	-2	-1	-1	-1	-1	0
100	0									

Formulae (1), (2), (3) were deduced from observations between 0° and 100°. Applied to temperatures below 0°, they give the following values, which are liable to the uncertainty attending extrapolation:

	$t_H - t_T$	$t_H - t_{16}$	$t_H - t_{59}$
- 5°	0°·03	0°·04	0°·02
- 10	·07	·08	·04
- 15	·12	·13	·07
- 20	·17	·19	·10
- 25	·23	·25	·14
- 30	·30	·32	·18
- 35	·38	·40	·23

**124. Compensated After-working.** Two glasses of unequal after-working can be so combined, in the construction of a mercury thermometer, that the after-working of the one is compensated by that of the other. To attain this end, the bulb must be made of the glass of smaller after-working, and a properly calculated volume of the glass of greater after-working must be placed inside it. Compensation thermometers on this plan were first introduced by Schott. W. Hoffmann published observations taken with such instruments, and at the same time deduced the relation which connects their change of zero with the after-working of the

two glasses.<sup>1</sup> G. Müller of Ilmenau has since published some researches on compensation-thermometers, and prepared the way for introducing them into practice.<sup>2</sup>

**Calculation of Depression.**<sup>3</sup> Let  $v_1$  denote the internal volume of the first or outer glass, measured up to the zero mark, and at the temperature zero;  $v_2$  the volume at zero of the second glass; and therefore  $v_1 - v_2$  the volume of the space originally occupied by the mercury at zero. Let both glasses have the same mean coefficient of cubic expansion  $\beta$  from  $0^\circ$  to  $t^\circ$ . Also let  $k$  stand for  $\frac{\gamma - \beta}{1 + 100\beta}$ ,  $\gamma$  being the mean coefficient of expansion of mercury from  $0^\circ$  to  $t^\circ$ . Then, if  $d_1$  be the depression of zero which would be produced in a thermometer of the first glass by heating to  $t^\circ$ , the volume of this depression, in a thermometer containing volume  $v_1$  of mercury at zero, is  $kv_1d_1$ ; since  $kv_1$  is the volume of a degree at zero (Art. 121). Similarly, the volume of the depression  $d_2$  in a thermometer of the second glass, containing  $v_2$  of mercury at zero, is  $kv_2d_2$ . In the compensation thermometer, the volume up to the zero mark, which was initially  $v_1 - v_2$ , is increased by  $kv_1d_1 - kv_2d_2$ ; also the volume of a degree at zero is  $k(v_1 - v_2)$ . Therefore, the depression, reckoned as usual in degrees, is

$$d = \frac{v_1d_1 - v_2d_2}{v_1 - v_2}.$$

The depression vanishes if

$$v_1d_1 - v_2d_2 = 0, \text{ or } \frac{v_1}{v_2} = \frac{d_2}{d_1}; \dots\dots\dots (4)$$

and when it does not vanish, its sign is the same as that of  $v_1d_1 - v_2d_2$ .

From what is known of the properties of glasses suited for this purpose, it may be expected that  $d_2/d_1$  will increase with  $t$ . As  $v_1/v_2$  is constant, it follows that, if the compensation is exact at a temperature  $t$ , the depression will be negative for higher temperatures, and positive for lower temperatures; in other words the thermometer will be under-compensated for lower and over-compensated for higher temperatures.

<sup>1</sup> *Zeitschr. f. Instrum.*, 17. 257 (1897).

<sup>2</sup> *Zeitschr. f. angewandte Chemie*, 1898, Heft 2.

<sup>3</sup> [Shortened and simplified.]

**Actual Construction.** In the compensation thermometers hitherto made, the outer glass has been the normal-thermometer glass 16<sup>III</sup>. For the inner, a glass has been specially prepared, called 335<sup>III</sup>. It has the percentage composition

SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>5</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Mn <sub>2</sub> O <sub>3</sub>
67.1	7.0	5.0	3.0	0.3	8.5	9.0	0.1

Its expansion is nearly the same as that of 16<sup>III</sup>, and its proportions of potash and soda ensure large after-working.

If the inner glass were left free to move about in the bulb, it would give rise, at any place where it touched the outer glass, to sharp angles in the intervening space surrounding the point of contact, and the mercury would be drawn out of these angles by surface tension, thus diminishing the effective volume of the bulb, and causing the mercury to stand too high in the stem. The construction which has been adopted is shown in fig. 27.<sup>1</sup> Hoffmann states that the attachment of the glass pillar, in the position indicated, presents no difficulty to the glassworker, and that it is not difficult to give the volumes the prescribed ratio. Müller on the other hand remarks that special precautions are necessary for obtaining the desired ratio of volumes.



Fig. 27.

**Observations.** Hoffmann observed, in an enclosure-thermometer, constructed in the ordinary way of glass 335<sup>III</sup>, a depression 0°·22 to 0°·23, after half-an-hour's heating at the boiling point of water. Comparing this with the corresponding depression in normal glass thermometers, which is 0°·05, we obtain, for the volume-ratio in a compensation-thermometer of these two glasses,

$$\frac{v_1}{v_2} = \frac{.225}{.05} = 4.5.$$

This conclusion has not yet been tested by the construction of a compensation thermometer with this volume-ratio; but Hoffmann tested nine instruments which had the following volume-ratios:

No. of thermometer	64	66	62	71	73	61	65	67	68
$v_1/v_2$	7	7	9	9	9	11	11	11	11

<sup>1</sup> Hoffmann, *l.c.* 258.



These ratios are much larger than that above deduced; it would therefore appear (see page 301) that the temperatures for which they were truly compensated were much higher than  $100^{\circ}$ . To permit of their exposure to these temperatures, they were provided with vacuous enlargements at the upper end of their tubes. Previous to the observations, the instruments were kept at over  $300^{\circ}$  for several days; a treatment which produced considerable elevations of their zeros.

The observations began with a determination of zero, followed by maintenance for about half-an-hour at about  $300^{\circ}$ . Then came another determination of zero, succeeded by another on the same day, and another the next day.

In the heating at  $300^{\circ}$ , some mercury distilled over into the enlargement at the top of the tube, and had to be subsequently brought back to the bulb. This circumstance vitiated the determination of the depression immediately produced by the heating; but good observations were made of the gradual change of zero during several days of rest which followed. The time of rest varied from 7 to 25 days, and was too short, in comparison with the intensity of the heating, to give full information. The observations included, in each case, one at the beginning and one at the end, of the time of rest.<sup>1</sup>

Seven experiments of this kind were made with thermometers 64 and 66. In one experiment there was no change of zero in 11 days; in the other six experiments, the zero fell, by from  $0^{\circ}01$  to  $0^{\circ}05$ , in from 7 to 18 days. This shows that the volume-ratio  $v_1/v_2 = 7$  gave over-compensation for heating to  $300^{\circ}$ .

Better results should therefore be expected from numbers 62, 71, and 73, which had  $v_1/v_2 = 9$ . No. 62 in fact showed a rise of  $0^{\circ}01$  in its zero after 1 day of rest; but this rise had disappeared after 18 days' rest. It would seem that after-working ceases sooner in glass 16<sup>III</sup> than in 335<sup>III</sup>. In four experiments with these three thermometers, 7 to 25 days of rest showed no change of zero; in four others 7 to 18 days of rest showed a fall of  $0^{\circ}02$ .

Very similar results were exhibited by Nos. 61, 65, 67, and 68, which had  $v_1/v_2 = 11$ ; there was no distinct evidence that they were under-compensated. The exactness of the assumed volume-ratios does not appear to have been submitted to any after tests.

<sup>1</sup>*l.c.* 259.

Adopting the supposition that a volume-ratio  $v_1/v_2 = 10$  would compensate the after-working due to heating at  $300^\circ$ , it follows, from equation (4), that for this temperature, the ratio of the after-workings of the two glasses is  $d_2/d_1 = 10$ . This is between two and three times the value of  $d_2/d_1$  for  $100^\circ$ . It is, however, not improbable that the final maximum of the depression-constant of 335<sup>III</sup> is larger than the value which was adopted, from experiments of comparatively brief duration.

**125. Elastic After-working.** Gustav Weidmann<sup>1</sup> undertook an investigation of the relations between elastic after-working in glass and its chemical composition. His observations include 13 different glasses. Twelve of them are Jena glasses, which have been already mentioned (p. 244) among thermometric glasses, under the designations II., IV., V., VII., VIII., X., XI., XIX., XXII., 16<sup>III</sup>, 17<sup>III</sup>, 18<sup>III</sup>. The 13th is a Thuringian glass, having the composition

SiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>
68.69	5.87	7.32	15.72 <sup>2</sup>	2.11

The meaning to be attached to the phrase *elastic after-working* is an extension, suggested by Abbe, of the meaning of the term *after-working* in thermometry. An antecedent deformation leaves behind it a residue, which only gradually subsides when the body is left to itself. *The ratio of this residue, after given time, to the antecedent deformation, is the measure of the elastic after-working.*

**Flexure Experiments.** The first measurements of this after-working were made by bending glass rods (strictly speaking, stout capillary tubes).

The following was the mode of procedure. The rod was firmly clamped near one end, and was at the same time supported on a knife-edge about 58 mm. from the clamp. Near the other end, a weight was hung on by a thread. In the later experiments, this loading lasted 10 minutes. The free end of the rod carried a fine scale 1 cm. long, which, when the rod bent, moved across the field of view of a horizontal microscope. The displacement of the end could thus be measured in thousandths of a millimetre, with an error not exceeding  $2\frac{1}{2}$  thousandths. The

<sup>1</sup> *Dissert.*, Jena, 1886.

<sup>2</sup> Weidmann gives 5.72, which appears to be a misprint.

readings were taken at 10, 20, 40, 60, 90 . . . seconds after loading.

Preliminary trials showed that after-working, as above defined, was independent of the amount of bending, and also independent of the dimensions of the rod. It accordingly depends only on the nature of the glass, and the duration of the loading. Results are therefore comparable, provided that the durations of loading are equal.

If a light loading was immediately succeeded by a heavy loading, the after-working showed an increase. If, however, several successive observations were made with this heavy loading, the after-working diminished again, and, after about three observations, resumed and retained its original value. Transition from heavy to light loading gave, as was to be expected, precisely the opposite result.

Experiments with one and the same kind of glass, at different temperatures, kept steady during the continuance of an experiment, showed that glasses resemble caoutchouc in having decrease of after-working with increase of temperature.

It was therefore necessary to conduct all experiments at the same temperature, as nearly as circumstances permitted. The long continuance of the investigation made the rigorous fulfilment of this requirement impossible.

The disappearance of deformation from the unloaded rod was hastened by warming, and also by tapping.

Tapping (and probably also warming) the loaded rod increased the after-working.

**Results.** The course and magnitude of after-working in the different glasses, as deduced from the flexure experiments, are given in the following table :

AFTER-WORKING.

After.	IV.	II.	X.	18 <sup>III</sup>	V.	XI.	16 <sup>III</sup>
20 secs.	·0011	·0018	·0027	·0036	·0036	·0038	·0065
40 „	06	08	21	24	28	25	45
60 „	04	05	17	15	22	19	33
90 „	03	03	14	11	18	13	25
120 „	—	—	10	08	14	09	19
180 „	—	—	08	05	10	05	14
Temperature.	11°	3°	4°	8°	4°	12°	7°

## AFTER-WORKING.

After.	VIII.	XIX.	VII.	Thuring.	XXII.	17 <sup>III</sup>
20 secs.	·0082	·0085	·0088	·0106	·0150	·0323
40 „	57	57	73	95	138	259
60 „	42	40	59	84	124	221
.90 „	30	27	47	75	113	185
120 „	22	19	37	66	94	157
180 „	14	11	23	57	85	128
Temperature.	10°	4°	3°	1°	16°	3°

In the last five glasses, the decrease of after-effect was followed still further, with the results shown below.

## AFTER-WORKING.

After.	XIX.	VII.	Thuring.	XXII.	17 <sup>III</sup>
3 minutes.	·0011	·0023	·0057	·0085	·0128
5 „	05	14	39	75	96
7 „	—	—	—	—	79
10 „	—	—	21	54	57
15 „	—	—	—	42	32
Temperature.	4°	3°	1°	16°	3°

**Piezometric Experiments.** Two thermometers, one of the above-mentioned Thuringian glass, and the other of the normal thermometer glass, 16<sup>III</sup>, were tested by internal pressure. They had spherical bulbs of diameters 36·2 and 32·2 mm., and tubes of internal diameters 0·27 and 0·45 mm., open at the top. The open end of the thermometer under experiment was connected, by a sealing wax junction, with a glass tube bent twice at right angles, which passed through the cover of the piezometer; and there was another opening in the cover through which the tube of a manometer passed. Pressure applied to the water which filled the piezometer was thus transmitted to the interior of the thermometer, producing dilatation of the bulb and tube, which was indicated by the depression of the mercurial column. The pressures employed were from 1 to 10 atmospheres, and



each pressure was kept on for 10 minutes at a time. The displacement of the summit of the mercury was observed with a reading microscope.

The most important precaution to be attended to in such experiments is that they be executed at a constant temperature. With this view the thermometer bulb was surrounded with snow in the caking condition. But as an experiment sometimes lasted three hours, the influence of the temperature of the surroundings was not quite excluded. It is probably the chief source of inaccuracy in the determinations. Another source is the long time required to take off the pressure, amounting to from 10 to 40 seconds.

In accordance with the definition above given of the numerical measure of after-working, Weidmann records the ratio of the remaining dilatation to the original dilatation after the lapse of stated times. He concludes from his observations that this ratio is constant for one and the same thermometer; and gives the following comparison of elastic after-workings as determined by the two different methods—flexure and dilatation :

Time in seconds.	Glass 16 <sup>III</sup> .		Thuringian.	
	Flexure.	Dilat.	Flexure.	Dilat.
20	·0065	·0069	·0106	·0107
40	45	56	95	92
60	33	45	84	85
90	25	36	75	77
120	19	29	66	66
180	14	20	57	57
Temperature.	7°	0°	1°	0°

For the Thuringian glass the two methods of deformation give nearly identical results. Weidmann inclines to the view that the larger differences in the case of the 16<sup>III</sup> are due to larger errors of observation.

**Torsion Experiments.** Lastly, Weidmann tested the after-working of two glasses—16<sup>III</sup> and 18<sup>III</sup>, by torsion. He used glass fibres, which, at the definite temperature, were first subjected for ten minutes to torsion, and then relieved. The apparatus

employed exactly resembled that described by Kohlrausch, and the readings were taken by telescope and scale. Within certain limits the experiments confirmed his result that the original and the remaining torsion are proportional; their ratio is taken as the measure of the after-working. The results are given in the following table, along with those of the other two methods, which are reproduced for comparison :

Time in seconds.	16 <sup>III</sup> .			18 <sup>III</sup> .		Thuring.	
	Flex.	Dilat.	Tors.	Flex.	Tors.	Flex.	Dilat.
20	·0065	·0069	—	·0036	—	·0106	·0107
40	45	56	·0055	24	·0024	95	92
60	33	45	45	15	21	84	85
90	25	36	36	11	18	75	77
120	19	29	31	08	14	66	66
180	13	20	24	05	12	57	57
Temperature.	7°	0°	0°	8°	0°	1°	0°

The comparison seems to indicate that the magnitude of after-working is not independent of the nature of the deformation.

**Formula for the Progress of After-working.** F. Kohlrausch, in accordance with a theory of after-working developed by Boltzmann, represents the falling off of the after-effect by the formula

$$x = Ce^{-at^m}$$

$x$  denoting the amount of deformation remaining after time  $t$ , reckoned from the instant when the body is set free, divided by the original deformation. For a given body, and given kind of deformation, the constants  $C$ ,  $a$ , and  $m$  are independent of the magnitude of the deformation, if not too great.

Weidmann finds that his flexure observations on glasses V. and VII. and Thuringian glass are well represented by the formula, with the following values of the constants :

	V.	VII.	Thuringian.
$C$ - -	0·005 980	0·016 04	0·016 86
$a$ - -	1	1	0·696 7
$m$ - -	0·573 1	0·552 6	0·416 7

On the other hand, his torsion observations cannot easily be reconciled with the formula.

**126. Elastic After-working and Chemical Composition.**

Of the 13 glasses tested for elastic working by Weidmann,

- 4 are potash glasses, viz., IV., V., XI.; 18<sup>III</sup>;  
 5 are soda glasses, „ II., VIII., X., 16<sup>III</sup>, XIX.;  
 1 is a lithia glass, „ VII.;  
 3, viz., 17<sup>III</sup>, XXII., and Thuringian, are mixed glasses in  
 the sense of containing both potash and soda.

The observations in Art. 125 show that the three mixed glasses are distinguished from the others by the largeness of their elastic after-working, and the lithia glass comes next to them. The following figures relate to the three mixed glasses:

	Thuring.	XXII.	17 <sup>III</sup> .
After-effect after 20 <sup>s</sup> ,	·0106	·0150	·0323
Ratio, $\frac{\text{Soda}}{\text{Potash}}$	$\frac{5\cdot87}{7\cdot32}$	$\frac{14}{14}$	$\frac{15}{10\cdot9}$

In the initial stage, the lithia glass shows after-working comparable with (though less than) that of soda glass, but its falling off is much more rapid.

The following figures show that the order from less to greater is nearly the same for content of soda as for after-effect:

	II.	X.	16 <sup>III</sup> .	VIII.	XIX.
Effect after 20 <sup>s</sup> ,	·0018	·0027	·0065	·0082	·0085
Percentage of soda,	7	8	14	15	15
Temperature,	3°	4°	7°	10°	4°

Taking temperature into account, VIII. ought to be regarded as having more after-working than XIX. It also shows a slower falling off.

The after-effect for potash glasses, even in the early stage, is very much smaller than that of soda glasses in the middle stage. The order from less to greater in content of potash is not the same as the order from less to greater in after-effect, and would not be made the same by correcting for difference of temperature. This is shown by the following figures:

	18 <sup>III</sup> .	IV.	V.	XI.
Percentage of potash,	9	13·5	16	18
Effect after 20 <sup>s</sup> ,	·0036	·0011	·0036	·0038
Temperature,	8°	11°	4°	12°

**127. Comparison between Elastic and Thermal After-working.** Weidmann's investigations, which we have been describing, were mainly directed to answering the question whether any relation can be found between elastic and thermal after-working.

Taking as an index of thermal after-working the depression-constant  $D$  defined in Art. 111, and noting its values for the groups of glasses which we have just been discussing, we have the following list of values of  $D$ , in decimals of a degree:

			Thuring.	XXII.	17 <sup>III</sup> .
Mixed glasses,	-	-	·50	1·05	1·06
Lithia glass,	-	-	·10	—	—
	II.	X.	16 <sup>III</sup> .	VIII.	XIX.
Soda glasses,	·02	·09	·05	·08	·07
		18 <sup>III</sup> .	IV.	V.	XI.
Potash glasses,	-	-	·05	·09	·09

These figures bear out the statement (see Art. 111) that mixed glasses show larger thermal after-working than glasses with only one alkali. The same is true, as we have just been showing, for elastic after-working. Looking upon after-working of either kind as a thing to be avoided, we may therefore say, with Weidmann, that "thermally bad" glass is "elastically bad," and that "elastically bad" glass is "thermally bad." The same conclusion results from comparing flexure observations with depression.

No exact relations between elastic and thermal after-working are however to be gathered from these comparisons, and it was to obtain further indications in this direction, that Weidmann undertook the piezometric experiments, in accordance with the following line of thought.

Let  $v_0$  be the volume of mercury in a thermometer at  $0^\circ$ ,  $\gamma$  and  $\beta$  the mean coefficients of expansion of the mercury and the glass from  $0^\circ$  to  $100^\circ$ . Then the capacity of the bulb is greater at  $100^\circ$  than at  $0^\circ$  by  $100\beta v_0$ , the volume of a degree at  $100^\circ$  is  $(\gamma - \beta)v_0$ , and hence the increase of volume is equivalent to  $\frac{100\beta}{\gamma - \beta}$  degrees. Call this number  $n$ ; then internal pressure producing an increase of volume measured by  $n$  degrees will afford a fair comparison, in its after-effect, with the depression  $D$



produced by heating from  $0^{\circ}$  to  $100^{\circ}$ . The piezometric results were, however, in the meantime only employed for comparison with the results from flexure.

Weidmann expresses a suspicion that thermal and elastic after-working cannot be comparable, inasmuch as elastic after-effects disappear quickly, whereas the vanishing of depression is a very tedious process. He also contrasts Pernet's law (Art. 113), that the depression produced by heating from  $0^{\circ}$  to  $t^{\circ}$  is proportional to the square of  $t$ , with the fact that elastic after-effects are simply proportional to the original deformation.

**128. On the Theory of the Thermal After-working of Glass.** The phenomenon of depression, which is found in all mercury thermometers, has not yet received a satisfactory explanation.<sup>1</sup> There can be no doubt that depression indicates an increase in the capacity of the bulb; but the cause of the increase is still an open question.

Under these circumstances we may be permitted, without pretending to offer a complete theory, to give a few indications as to the nature of the actions whose existence can be inferred from the observations.

The after-working which is in question includes a series of phenomena. The first of them is, that when a glass is raised from  $0^{\circ}$  to  $t^{\circ}$ , its volume, while maintained steadily at this temperature, goes on increasing for a considerable time. A good example is furnished by Wiebe's observations on the continually advancing depression of a boiling point thermometer of Thuringian glass in alcohol vapour (Art. 115). The continual increase depends (for any given glass) not only on the temperature  $t$  to which the thermometer is raised, but also on the progress of the heating up to that temperature.

**Deformation of the Walls of a Hollow Vessel by Heating.** When an approximately spherical or cylindrical hollow vessel, with its walls originally free from stress, is rapidly raised in temperature from  $0^{\circ}$  to  $t^{\circ}$ , it is obvious that, during the rise, the walls will consist of layers of different temperatures. If we imagine the connections between the layers to be dissolved, the

<sup>1</sup>A brief account of attempted explanations is given by R. Weber in the introduction to his investigation of the influence of the composition of the glass on depression. *Ber. d. Berlin Akad.*, Nov. 1883.

layers would separate from one another, to distances increasing with the differences of temperature, and with the expansibility of the material. As soon as all the layers have attained the common temperature  $t^\circ$ , they will, for the first time, be all in contact, and free from stress. The capacity of the vessel when this condition is attained, may be designated its *normal* volume.

As the layers are actually united firmly together, it follows that, during the rise of temperature, they deform each other; the outer layers are subjected to thrust, the inner ones to pull, and between the two there will be a layer free from stress. In spherical or cylindrical vessels, the deformations thus produced could be calculated, if the thermal expansibility of the material, and its coefficients of elasticity, were known, and if a definite assumption were made as to the distribution of temperature from layer to layer.

**After-working of this Deformation.** It cannot be doubted that the elastic deformations thus called out in the walls during the rise of temperature produce after-working. The circumstance that the deformations are accompanied by rise of temperature has probably an influence on their magnitude and course, and renders their estimation more difficult.

Weidmann's observations (Art. 125) furnish a basis of calculation for the after-working of the dilatation, if we employ the assumption (which was supported by his flexure observations) that after-working is increased by warming during the application of stress.

No data are available for the after-working called out by thrust. Whether it is influenced—and if so in which direction—by rise of temperature during the application of stress, is not known.

The ratio of these two after-workings one to the other is also not indicated by available observations. Moreover it is quite possible that the coefficients of expansion of the different layers are slightly modified by the conditions of tension and thrust.

**Influence of After-working on Capacity.** It is not *à priori* probable that the layers, affected as they are with opposite after-workings of varying intensities, should, on attaining the permanent temperature  $t^\circ$ , be in permanent equilibrium, and have their normal volumes. The gradual relief of the stresses in the layers is not likely to be brought about without changes in the volume of the vessel. It would not be altogether unreasonable to suppose

that there might even be alternate inward and outward movements, as results of the two opposite kinds of stress, which contend with one another. Lack of experimental evidence forbids confident statements on these matters, and we can only form conjectures.

**Hypothesis on Thermal After-working.** As a working hypothesis, let us assume that these supposed movements actually occur, and bring about the observed thermometric depression. The following will then be the course of events.

After the temperature  $t^\circ$  is reached, the after-working of thrust in the outer layers first comes into operation, and the vessel regains its normal capacity. The movement continues beyond this position, and the after-working of pull in the inner layers comes into play. The limit of this movement will be determined, on the one hand by the magnitude of the after-working itself, and on the other by the elastic resistance of the outer layers. After the movement of extension has ceased, there will be a slow recoil, the after-working of pull vanishes gradually, and finally the normal volume is attained, but this time without stress in the walls.<sup>1</sup>

From this view of what occurs, it will immediately follow that the conditions which promote largeness of depression in a glass are, large thermal expansibility, large after-working from pull, small conductivity, and small coefficients of elasticity.

**Verification of these Conclusions.** These conclusions, as to the physical properties which conduce to largeness of depression of the zero of a thermometer subjected to rapid heating, can be tested by comparison with observed depressions.

Pernet has laid down the rule that, in order to obtain agreement between the indications of thermometers which have unequal depressibilities, the observed reading must be compared with the zero as determined immediately after.<sup>2</sup>

<sup>1</sup>[Whether we accept or reject this outline of successive stages, it seems clear that, taking as independent variables (1) thermal expansibility, (2) thermal diffusivity, (3) resistance to distortion, (4) liability to mechanical after-working—which nearly correspond to  $B$ ,  $K$ ,  $E$ ,  $N$ ,—the distortion produced by sudden change of temperature of the surface will increase with the largeness of (1), and with the smallness of (2) and (3). The after-working consequent on the distortion will naturally be proportional jointly to the distortion and to (4). We thus arrive at the conclusion stated in the text.—J. D. E.]

<sup>2</sup>Winkermann, *Handb. d. Physik.*, II. 2. 34.



Hence we must infer that the depression brought about by heating from  $0^{\circ}$  to  $100^{\circ}$  is not much changed by the immediately subsequent cooling from  $100^{\circ}$  to  $0^{\circ}$ . As regards the physical qualities above indicated as affecting depressibility, the following facts may be adduced.

Weidmann found a connection between depression and the elastic after-working brought about both by bending and by internal pressure—a connection which he expressed by saying that “a thermally bad glass is also elastically bad, and *vice versa*.” The absence of a definite quantitative relation is only what was to be expected, if depressibility depends on other qualities as well.

The opinion that smallness of thermal expansibility keeps down depressibility has been long held, and is borne out by even a superficial comparison of coefficients of expansion with after-workings resulting from internal pressure. In giving an account of the thermal after-workings of 16<sup>III</sup>, 17<sup>III</sup>, and 18<sup>III</sup>, Weidmann calls attention to the great differences in expansibility between these three glasses.<sup>1</sup> In fact, if depressibility is to be made small, it is absolutely necessary to employ glass of small expansibility.

Conductivity has also been long regarded as influencing thermal after-working. In citing old researches by Wild, Weidmann expresses the belief that “bodies which conduct heat well have small thermal after-working.”<sup>2</sup> This explains the absence or extreme smallness of thermal after-effects in metals.

Furthermore, it is not merely internal conductivity that must be regarded as influential. The difference of temperature between the external and internal surfaces of a bulb when exposed to heating, will depend mainly on the ratio of surface conductivity to internal conductivity. An experiment of Weidmann's seems to show that different kinds of glass differ largely in surface-conductivity. When steam was passed through tubes of 16<sup>III</sup>, 17<sup>III</sup>, and 18<sup>III</sup> for the purpose of heating them, 16<sup>III</sup> and 18<sup>III</sup> were quickly bedewed, but not 17<sup>III</sup>, although, as he goes on to remark,<sup>3</sup> it was a hygroscopic glass. Clearly, the surface of the hygroscopic glass was more quickly heated up than the surfaces of the others; which is easily intelligible, as steam was the heating substance. In internal conductivity it was intermediate between the other two.

<sup>1</sup> *Diss.*, 18.

<sup>2</sup> *Diss.*, 34.

<sup>3</sup> *Diss.*, 18.



The influence of elasticity upon depressibility seems never to have been suggested. There is, therefore, special need for evidence on this point.

The following table will serve for testing the foregoing conclusions. The first column gives the names of the eleven glasses. In the second column,  $\beta$  is the coefficient of cubic expansion. In the third,  $K$  is the internal conductivity, in C.G.S. units. In the fourth,  $N$  is the measure of the after-effect 20<sup>s</sup> after unloading, in the flexure experiments.  $E$  in the fifth column is Young's modulus of elasticity; and  $D$  in the last column is the depression

Name.	$10^7 \beta$ .	$10^3 K$ .	$10^4 N$ .	$E$ .	$D$ .
II.	328	1.490	18	8490	0° 02
IV.	253	2.081	11	6595	0 08
V.	233	1.504	36	5980	0 09
VIII.	281	2.260	82	6865	0 08
X.	237	1.630	27	7180	0 09
XI.	231	1.728	38	7280	0 09
16 <sup>III</sup>	241	2.100	65	7543	0 05
17 <sup>III</sup>	342	1.869	323	6781	1 06
18 <sup>III</sup>	162	1.588	36	7810	0 05
XIX.	271	1.690	85	8050	0 07
XXII.	342	1.882	150	6454	1 05

after heating from 0° to 100°. All the values of  $N$  and of  $D$  are from direct observation. Most of the other values are computed from the chemical composition of the glasses (see Arts. 97, 93, 72); the only observed values being  $\beta$  for 16<sup>III</sup>, 17<sup>III</sup>, 18<sup>III</sup>, and  $K$  and  $E$  for 16<sup>III</sup>. The values of  $N$  were all observed at the same temperature. The values of  $D$  are not rigorously comparable, inasmuch as the thermometers were not all of the same age. As there are here several elements of uncertainty, inferences must be drawn with caution, and not based on small differences.

A conspicuous example of the influence of elasticity is furnished by the first two glasses II. and IV., the former a soda and the latter a potash glass. Both of them show small elastic after-working; IV. has the smaller coefficient of expansion, and much the larger conductivity. These are reasons for expecting it to have the smaller depressibility; and the fact that its depression-constant is four times as large as that of II. can only be

accounted for by the fact that it has a coefficient of elasticity rather below the average, while that of II. is the largest in the list. The comparison of VIII. with XIX. furnishes another example of the influence of elasticity.

The influence of conductivity is seen by comparing VIII. with X. The influence of the coefficient of expansion (as well as of the coefficient of elasticity) is brought out by the comparison of 18<sup>III</sup> with the group V., X., XI. The equality of the depressions for these three glasses is not quite in accordance with theory—we should expect that of V. to be the largest—and the discrepancy is perhaps to be ascribed to errors in the values deduced from chemical composition.

Comparisons of this kind could easily be multiplied. In the great majority of cases they are in harmony with the predictions of the foregoing theory.

**129. Thermo-elastic After-working.** In Art. 73, in connection with the elasticity of glass at high temperatures, it was mentioned that Winkelmann found indications of an increase in the coefficients of elasticity of glasses, after heating and cooling down again. He illustrates the point<sup>1</sup> by a series of observations on glass 23 (in his own numbering). On April 27, 1894, after a determination of its coefficient of elasticity on the previous day, it was heated to 380°; and, being tested on April 28, showed a larger value of the coefficient, which, however, had fallen off a little by April 29; and on May 19 the fall had reduced it to nearly its original value. Being then heated to 480°, it was found on May 30 to have nearly returned to its original value; but being then again heated to 480°, the increased value which it showed remained steady till June 14.

Several glasses were treated in this way until the increased coefficient of elasticity became steady; and these steady values are given, together with the original values, in the following table. They are in kg. per sq. mm., for the temperature 20°. The column headed W. contains Winkelmann's numbers for the glasses. The differences are given in percentages, and range from 0.1 to 4.6 per cent.<sup>2</sup>

<sup>1</sup> *Ann. d. Phys. u. Chem.*, 61. 114 (1897).

<sup>2</sup> The value 7563 given in Art. 72 for glass 19 is the mean of observations on three rods; 7540 is the value for one of these rods.

The table does not furnish exact comparisons between the glasses; inasmuch as they were not all heated to the same temperature. The increased values were not, in a strict sense,

W.	Before.	After.	Diff.	W.	Before.	After.	Diff.
19	7540	7672	1.8 %	33	5477	5494	0.3 %
21	5468	5606	2.5	34	7180	7349	2.3
22	4906	5023	2.4	35	7314	7524	2.9
23	7992	8146	1.9	38	7465	7649	2.5
24	5426	5433	0.1	84	7401	7564	2.2
25	6766	6983	3.2	85	7416 <sup>1</sup>	7589	2.3
26	5461	5505	0.8	86	6097 <sup>1</sup>	6218	2.0
28	6599	6669	1.1	87	7971	8340	4.6
29	6638	6650	0.2	88	7461	7551	1.2
30	6014	6159	2.4	89	7180	7234	0.7
31	6373	6441	1.1	91	6572 <sup>1</sup>	6687	1.7
32	5843	5885	0.7				

permanent. After the lapse of a long time smaller values were found, which gradually diminished to the original values. In glass 19, for example, this complete return occurred after about 16 months; in glasses 85 and 87 after about 10 months.

Thermoelastic after-working is not, by any means, a property peculiar to glass. Winkelmann has found very conspicuous manifestations of it in platinum.<sup>2</sup> A strip of platinum, of the same thickness as the wall of a thermometer bulb, showed an initial coefficient of elasticity of 16926 kg. per sq. mm. After several warmings to 20°, this had increased to 18380—an increase considerably larger than that observed in glass. After a rest of 10 months, the coefficient had gone back to 17516; and it showed little further decrease during the next 4 months.

The observed phenomenon cannot be a mere consequence of increase of volume; for this is too small to account for the observed difference, as Winkelmann has pointed out, both in the case of glass and of platinum. A thermometer made by L. Marchis, with a glass tube melted on to a platinum bulb,<sup>3</sup> showed, after heating

<sup>1</sup> These three glasses had been in the heating apparatus before the first observation.

<sup>2</sup> *Ann. d. Phys. u. Chem.*, 63. 117 (1897).

<sup>3</sup> *Jour. de Phys.* (3) 4. 217 (1895).

to  $100^{\circ}$ , a depression so small that its existence could not be established with certainty. Still less is it possible to ascribe the effect to diminution of volume resulting from protracted heating; for, as Winkelmann has remarked, this would produce an apparent diminution of the coefficient of elasticity.

The increase is real, and not merely apparent. Winkelmann suggests, as the most obvious explanation, the introduction of stress by the heating and quick cooling; the glass being supposed to be previously well annealed. If this is the explanation, the stresses must, however, be different in kind from those produced by the rapid cooling of glass heated to softness; for Winkelmann and Schott have confirmed Quincke's result, that unannealed glasses have smaller coefficients of elasticity than well annealed.<sup>1</sup> Furthermore, the circumstance that the glasses were heated to near their softening points does not seem to be material; for the platinum showed similar effects after heating to  $400^{\circ}$ —a temperature very remote from its melting point.

<sup>1</sup> *Ann. d. Phys. u. Chem.*, 51. 710 (1894).



## CHAPTER X.

### CHEMICAL BEHAVIOUR OF GLASS SURFACES.

130. For glasses which are to be used in the construction of physical instruments or of chemical utensils, immunity from chemical attack, by any liquids, vapours, or gases which are likely to come in contact with them, is often a prime consideration. For instance, glasses possessing valuable optical properties may be unfit for use in optical instruments by reason of susceptibility to the action of damp air. Or, to give another illustration, it is well known that Stas, in his revision of the atomic weights of the elements, thought it necessary to have the glass vessels which were to be used in the research expressly made, of glass characterised by special power of resisting such influences.

The nature and course of the chemical actions produced on the surface of glass, by contact with various substances and under various conditions, and the dependence of these actions on the chemical composition of the glass, have been the subject of very numerous researches. We must confine our attention to those which are most closely related to the work of the Jena glass-making laboratory. They are contained in the following memoirs, which we give in chronological order, together with the abbreviated designations by which we shall refer to them :

M. I.=F. Mylius, "On Disturbances of Spirit Levels." Communication from Reichsanstalt. *Zeitschr. f. Instrum.*, 8. 267 (1888).

M. II.=F. Mylius, "Testing the Surface of Glass by Colour Reaction." Comm. from Reichs. *Zeitschr. f. Instrum.*, 9. 50 (1889).

Sch.=O. Schott, "Soaking of Water into Glass Surface." *Zeitschr. f. Instrum.*, 9. 86 (1889).

- M. u. F. I.=Mylius and F. Foerster, "Solubility of Glass in Water." *Ber. d. deutsch. Chem. Ges.*, 22. 1092 (1889).
- M. u. F. II.=Mylius and Foerster, "Solubility of Potash- and Soda-glasses in Water." Commun. from Reichsanstalt. *Zeitschr. f. Instrum.*, 9. 117 (1889).
- M. u. F. III.=Mylius and Foerster, "Determination of Small Quantities of Alkali, etc., in Water." Commun. Reichs. *Ber. d. deutsch. Chem. Ges.*, 24. 1482 (1891).
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**131. Decomposition of Surface of Glass by Water.** After attention had, for several years, been directed to the circumstance that glass levels in course of time became useless, owing to a rough coating which formed upon their inner surfaces, an investigation was undertaken by the Reichsanstalt into the cause of this trouble. It disclosed the fact that the phenomenon occurred in levels in which the ether was not free from water, and that it arose from chemical decomposition of the

surface of the glass by the water. In accordance with many earlier observations, it was found that the water had extracted potash and soda from the glass, while only a relatively small quantity of silicic acid had been dissolved.

The formation of the rough coating being thus traced to the decomposition of the glass by water, a comparison of the relative susceptibility of different glasses to this kind of attack was obviously suggested. Previous publications contained no comparisons from which quantitative conclusions could be drawn. Such a comparison was undertaken by Mylius, for 14 different glasses, among which were five Jena glasses, including the normal-thermometer glass 16<sup>III</sup>.<sup>1</sup>

The following was the method of procedure. The glass to be operated on was first pounded in an iron mortar, and, by the help of two sieves, was obtained in the form of rather coarse particles of nearly uniform size. A volume of 8.01 c.c. of this material was weighed, and put into 70 c.c. of distilled water in a platinum vessel, in which it was heated for five hours in a bath of boiling water. The platinum vessel carried a small back-flow condenser cooler, connected with a Liebig's potash apparatus for excluding atmospheric carbonic acid. The solution, when it had become cold, was filtered, and a volume of 60 c.c. of the filtrate was employed for the determination of the constituents. A defect, as regards comparability, is the absence of security for equality of the total surface of the glass particles in different experiments.

Mylius gives, in a table which we do not reproduce, the quantities (in milligrammes) of silicic acid, soda, and potash in each 60 c.c. of solution; and the quantities of oxygen in the soda and potash are calculated on the assumption that there are 16 parts by weight of oxygen in 62 of  $\text{Na}_2\text{O}$ , or in 94 of  $\text{K}_2\text{O}$ . The quantities of oxygen thus computed for the two alkalis are added, and the sum is adopted as the measure of susceptibility to attack by water. This gives the same order of arrangement as would be obtained by dividing the weight of soda by 62, the weight of potash by 94, and adding.

In the list of glasses thus arranged in order of susceptibility to attack, the first—that is, the most susceptible—is potash water-glass, and the second, soda water-glass. The pure silicates of

<sup>1</sup>M., I. 276.

potash and of soda respectively, were also tested for comparison. Flint glasses with a large content of lead were found to have specially high withstanding power. The densest Jena lead silicate, containing 78.3 per cent. of lead oxide, and 21.7 of silicic acid, came last in the list, being almost completely exempt from attack by water. It is known that these flint glasses are only very slightly hygroscopic, and that they are good insulators for electricity. On the other hand, they are easily decomposed by acids and alkalis.

The ratio of the constituents extracted from glass is not the same when the water is cold as when it is hot. Mylius found, in the case of soda water-glass, that water at 100° gave a solution containing 0.36 of a molecule of soda to each molecule of silicic acid, while water at 20° gave, after nine days' contact with powdered water-glass, a solution containing 3.1 molecules of soda to one of silicic acid.

**132. Testing of Surface by Colour-Reaction.** R. Weber has introduced a method of testing glasses by exposing them for 24 hours to an atmosphere of hydrochloric acid vapour, and afterwards to air.<sup>1</sup> The glass becomes covered with a rime of chlorides which is more abundant in proportion as the glass is more susceptible to attack. Weber himself carried out, by this method, a thorough investigation of the relation between the composition of glasses and their chemical behaviour under atmospheric influences.<sup>2</sup> The method requires a trained eye, and cannot be applied to rough surfaces, because the rime is generally not recognisable upon them.

Several attempts have been made to bring out the behaviour of glass by colour-reactions. The usual plan is to expose the surface to the contact of aqueous solutions of substances which change colour when acted on by alkalis. As the water draws out alkali from the glass, red solution of litmus is coloured blue where it is in contact with the glass; a colourless solution of phenol-phtalein or of haematoxylin becomes purple-red. Mylius endeavoured to utilise the blue colouring produced in a solution of starch and iodine by a trace of alkali; and he describes a pretty lecture experiment, in which the action of water on glass is rendered visible.<sup>3</sup> These reactions are suitable for

<sup>1</sup> M., II.<sup>2</sup> *Ann. d. Phys. u. Chem.*, 6, 431 (1879).<sup>3</sup> M., II. 51. 5.



showing that glass gives up alkaline constituents to water, but cannot well be employed for comparative testing of different glasses.

**The Iod-eosin Test.** If a glass surface is brought into contact with watery ether, it draws water from the solution and gives up alkali to it. On the other hand, the orange yellow colour of a solution of iod-eosin ( $C_{20}H_8I_4O_5$ ) in ether is changed by alkali into red. Mylius, who had previously used this colour reaction for another purpose,<sup>1</sup> has applied it to the practical testing of glasses. Commercial ether is shaken up with water at ordinary temperature, till it is saturated with water. It is then poured off from the rest of the water, and iod-eosin is added in the proportion of 0.1 gm. to 100 c.c. of the liquid. The solution is filtered, and can be preserved in well-closed flasks till wanted.

Glass vessels are tested by pouring in the solution. The first step is to clean the surface from any products of weathering which may adhere to it, by carefully rinsing it with water, with alcohol, and lastly with ether. Immediately after the cleansing with ether, the eosin solution is poured in, the vessel is carefully closed, and the solution is allowed some 24 hours to do its work. It is then emptied out, and the glass rinsed with pure ether. The surface of the glass is now seen to be coloured red; and the strength of the colour furnishes an indication of the susceptibility of the glass to attack by cold water.

Mylius tested in this way a number of the glasses of commerce, the vessels employed in the first instance being glass tubes. He gives a coloured plate showing the appearances presented by different specimens after the same treatment. The differences in the colouring are very considerable. They are however not due solely to differences of composition in the glasses. Inequalities of weathering, and other differences of condition in one and the same kind of glass, are also revealed to the eye by this very sensitive method.

A crystal glass with large content of lead was conspicuous for the strength of its colouring, although it did not give up much soluble material to water. The colour was partly produced by the lead salt of eosin, which remained clinging to the glass when the alkali salt of eosin was removed by rinsing with water.

<sup>1</sup> M., I. 269.

Normal-thermometer glass showed about the same colouring as the least fusible kinds of Thuringian glass. The weakest colouring was shown by the Bohemian glass from the works of Kavalier.

The eosin test agreed completely in its results with Weber's method.

Lastly, Mylius used the eosin test to show the effect of various modes of treatment, in increasing or diminishing susceptibility to decomposition. For details of these researches, in which the utility of the method is conspicuously shown, we must refer to the original memoir.<sup>1</sup>

**133. Penetration of Water into the Surface.**<sup>2</sup> Some specimens were handed over to Schott in 1883 by the Standards Commission, of thermometer tubes which, after being kept for several days in boiling water, had shown hook-shaped cracks going right through the walls, and, on the gentlest touch, broke into large pieces, which clung together. When Schott heated the pieces in a gas-flame to a temperature higher than that of boiling water, a thin layer of the outer surface resolved itself into small amorphous splinters, while the inner walls of the tube remained unaltered. Previous to the heating in the gas-flame, no visible changes could be detected in the surface. The appearances suggested that water, in contact with glass, not only dissolves components of the glass, but is taken in by the superficial layers. The water which has penetrated will, on sudden heating, be converted into steam, which produces the fine splintering.

To put this suspicion to the test, specimens of several kinds of glass, in the form of tubes and of small discs, were submitted to the action of hot distilled water, in a digester, on five consecutive days. They were then carefully cleaned, with water, alcohol, and ether successively; then dried for several hours over sulphuric acid; and then kept at 150° in an air bath. Three weighings were made, the first before exposure to the hot water; the second after the drying; and the third after the final heating in air. The losses of weight from the first to the second, and from the second to the third weighing, are given below, the percentage composition being prefixed. The losses of weight are expressed in mg. per sq. decim. of glass surface.

<sup>1</sup>M., II. 55.

<sup>2</sup>Sch.

## 1. INFERIOR THURINGIAN GLASS.

$\text{SiO}_2$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{CaO}$	$\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$	$\text{MgO}$
68.69	15.87	7.32	5.66	2.11	0.24

Losses of weight, 10.7 mg., 4.9 mg.

After the heating in water, the surface showed no change; after heating in air, at  $150^\circ$ , it was quite corroded, and fine scales came off in abundance. The loss, 4.9, was therefore not all water.

## 2. SUPERIOR THURINGIAN GLASS.

$\text{SiO}_2$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{CaO}$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{MgO}$
69.02	16.01	3.38	7.24	3.0	0.43	0.26

There was, in addition, a little manganese oxide, and arsenic acid. The glass was tested under three different conditions; (a) after keeping for two years in air; (b) after previous heating at  $100^\circ$ ; (c) after heating to the commencement of softening. The results were

(a) Losses of weight,	3.5 mg.,	0.8 mg.
(b) Losses of weight,	2.5	0.8
(c) Losses of weight,	1.8	0.6

In (a), the surface after the heating in water appeared absolutely unchanged. After the heating in air, it was all covered with fine scratches, but threw off no scales.

In (b), these scratches were very fine, and barely visible to the naked eye.

In (c), no scratches were visible, even with a magnifier.

## 3. JENA GLASS XVIII.

$\text{SiO}_2$	$\text{Na}_2\text{O}$	$\text{PbO}$	$\text{ZnO}$	$\text{B}_2\text{O}_3$
66	13	10	7	3

Losses of weight, 1.2 mg., 0.0 mg.

The surface showed a bluish shimmer, without other change.

## 4. JENA GLASS XXII.

$\text{SiO}_2$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{CaO}$
66	14	14	6

The glass, after only 36 hours' heating in water, already showed numerous irregular cracks, and began to go to pieces; the surface became rough. When heated to  $150^{\circ}$ , the surface flaked off, and the glass was marked all over with numberless scratches.

5. JENA GLASS 3<sup>III</sup>.

SiO <sub>2</sub>	Na <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>
62	16	16	2	4

Losses of weight, 5.5 mg., 0.0 mg.

The surface had assumed a bluish shimmer, without other change.

6. JENA GLASS 6<sup>III</sup>.

SiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>
73	15	5	5	2

Losses of weight, 0.9 mg., 0.7 mg.

The surface was unchanged.

7. JENA GLASS 15<sup>III</sup>.

SiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	ZnO
67	8	9	7	2	7

Losses of weight, 0.9 mg., 0.06 mg.

8. JENA GLASS 13<sup>III</sup>.

SiO <sub>2</sub>	K <sub>2</sub> O	ZnO	B <sub>2</sub> O <sub>3</sub>
58	15	20	7

Losses of weight, 1.6 mg., 0.24 mg.

These researches, as Schott points out, show clearly the superiority of soda to potash glasses.

If a laboratory utensil of common glass, that has seen much service involving long-continued contact with water, is brought into the gas-flame, its surface often becomes marked with fine scratches. Easily fused glasses containing potash and little or no lime, are capable of taking in so much water, even from the air,



that their surface, on heating, becomes full of scratches, as may be often seen in lamp chimneys that have lain for a long time unused.

Three Jena potash glasses, numbers 547, 564, 563, containing percentages 33, 35, 42 of potash, were found, after lying by for many weeks, to have taken in from the air so much water that, on heating, they showed extensive splintering. After lying by still longer, they were covered with a wrinkled skin, which could be scraped off with a knife. After some years, this skin, in the case of No. 563, had continually increased in thickness, and gradually came away from the sound glass beneath it, though it gave the impression of being solid. The detached coating, so far as it was not decomposed externally by carbonic acid, preserved its amorphous character perfectly. With protracted heating at from  $200^{\circ}$  to  $300^{\circ}$ , it swelled up and acquired a pumice-like structure.

Two glasses with large content of soda, namely No. 232, containing 45  $\text{SiO}_2$ , 20  $\text{Na}_2\text{O}$ , 35  $\text{BaO}_2$ ; and No. 107, a soda silicate glass, showed as little power of holding together as the glasses with potash in their composition. They became covered with a *crystalline* crust which was easily detached from the glassy core. Heating produced no change in the surface.

Similar observations have been made in many quarters, and have been collected by Foerster.<sup>1</sup> They relate to cases in which considerable quantities of water were taken up by glasses. According to Foerster,<sup>2</sup> water is always taken up where glass is acted on either by liquid water or by steam. The water enters into chemical combination with the glass, forming hydrated products.

According to this view, the action of water on glass is not a true process of solution, in which there is direct transition from the undissolved to the dissolved state; but rather a process of soakage, in which the passage, from the original solid substance, to the final dissolved products, is effected through a series of intermediate transformations. In water-glass, and other glasses containing very little lime, this process of soakage is especially conspicuous.

<sup>1</sup>F., II. 2920, and F., IV. 457, besides observations of his own in F., I. 2495.

<sup>2</sup>F., II. 2920, and F., IV. 458.

**134. Investigation of the Behaviour of Test-samples of Potash and Soda Glasses.**<sup>1</sup> In order to complete Schott's observations described in the preceding article, Mylius and Foerster carried out a comparative investigation of the action of water on test-samples, of systematic composition. Their memoir begins with an account of observations on water-glasses, from which we extract the following particulars.

The great affinity of potash water-glass for water reveals itself, under suitable conditions, by distinct generation of heat. Fifty grammes of pulverized potash water-glass, of composition  $K_2O \cdot 3 SiO_2$ , were well mixed with enough water to form a thick pulp, which was left to itself at the temperature  $18^\circ$ . In a quarter of an hour it had risen to  $32^\circ$ , and it remained at about this temperature for a long time. When the same glass, mixed with a little water, was warmed by means of a water bath of temperature  $55^\circ$ , the mixture rose in a few minutes to  $80^\circ$ ; and in about ten minutes the pulp had solidified into a homogeneous mass.<sup>2</sup>

To this property of potash water-glass Mylius and Foerster attribute its setting, like hydraulic cement, under water. The pulp formed by the swelling-up which occurs when it takes in water, cements together the as yet unhydrated particles of the powder. In a day or two it becomes a glassy mass, of the hardness of stone, containing up to 50 per cent. of water. When heated, it gives out this water with violent tumescence; and at a red heat it acquires the character of pumice.

Soda soluble-glass combines with cold water much more slowly. When reduced to powder, and kept under water, it takes two or three months to harden.

**The Meltings for Producing the Test Specimens** were carried out in a Seger gas furnace. The melting pots were made from a fireclay compounded by Heinecke. The glass took up less than 1 per cent. of alumina from them, and this impurity (the same for all) was neglected. The amount of a melting did not exceed 500 gm. Those of the glasses thus obtained which were included in the investigation, had the molecular compositions shown in the following list; the 6 molecules of  $SiO_2$  being common to all.

<sup>1</sup> M. u. F., I. and II.

<sup>2</sup> M. u. F., I. 1098.

6 SiO<sub>2</sub>

I.	2 K <sub>2</sub> O	II.	2 Na <sub>2</sub> O
III.	1 $\frac{3}{4}$ K <sub>2</sub> O, $\frac{1}{4}$ CaO	IV.	1 $\frac{3}{4}$ Na <sub>2</sub> O, $\frac{1}{4}$ CaO
V.	1 $\frac{1}{2}$ K <sub>2</sub> O, $\frac{1}{2}$ CaO	VI.	1 $\frac{1}{2}$ Na <sub>2</sub> O, $\frac{1}{2}$ CaO
VII.	1 $\frac{1}{4}$ K <sub>2</sub> O, $\frac{3}{4}$ CaO	VIII.	1 $\frac{1}{4}$ Na <sub>2</sub> O, $\frac{3}{4}$ CaO
IX.	1 K <sub>2</sub> O, 1 CaO	X.	1 Na <sub>2</sub> O, 1 CaO

This gives as their percentage compositions :

	SiO <sub>2</sub> .	K <sub>2</sub> O.	Na <sub>2</sub> O.	CaO.
I.	65.7	34.3	—	—
II.	74.4	—	25.6	—
III.	66.8	30.6	—	2.6
IV.	74.6	—	22.5	2.9
V.	68.0	26.7	—	5.3
VI.	74.8	—	19.4	5.8
VII.	69.3	22.6	—	8.1
VIII.	75.0	—	16.2	8.8
IX.	70.6	18.4	—	11.0
X.	75.3	—	13.0	11.7

The 10 specimens, in the form of coarse grains, were subjected to the action of hot water, the investigation being conducted on the same plan as Mylius' experiments, which we have described in Art. 131. The quantity operated on in each experiment was 7.74 c.c., this being the volume of 20 gm. of normal thermometer glass. To keep down the error arising from variations in the total area of glass-surface in contact with the water, care was taken, by repeated siftings, to ensure that there should be approximately the same number of grains to the cubic centimetre in all cases. The actual numbers ranged from 7300 to 7624 per c.c.

**The results** are given by Mylius and Foerster in a table, from which we reproduce an extract. The first column contains the distinctive numbers of the glasses; the second, the number of molecules of alkali to one molecule of silicic acid in the com-

position of the glass; the third, the quantity operated on, in grammes. The next three columns give the quantities of silicic acid, potash, and soda, found in the solution; and the last two columns are derived from these three by calculation; one of them giving the amount of oxygen contained in the dissolved alkali, and the other the number of molecules of alkali to one molecule of silicic acid in the solution; the volume of the solution being in each case 60 c.c. The number of milligram equivalents of alkali in the solution can be found by dividing the numbers in the last column but one by 16.

Number.	To 1 SiO <sub>2</sub> .	Quantity.  gm.	In 60 c.c. of solution.				
			SiO <sub>2</sub> .	K <sub>2</sub> O.	Na <sub>2</sub> O.	Oxygen in alk.	To
			mg.	mg.	mg.	mg.	1 SiO <sub>2</sub> .
I.	0.33 K <sub>2</sub> O	18.824	4246.8	2377.2	—	404.6	0.36 K <sub>2</sub> O
II.	0.33 Na <sub>2</sub> O	18.979	2144.7	—	842.4	217.3	0.38 Na <sub>2</sub> O
III.	0.29 K <sub>2</sub> O	18.948	2997.6	1675.8	—	285.24	0.36 K <sub>2</sub> O
IV.	0.29 Na <sub>2</sub> O	18.979	303.9	—	202.8	52.33	0.64 Na <sub>2</sub> O
V.	0.25 K <sub>2</sub> O	19.002	65.1	158.4	—	26.92	1.56 K <sub>2</sub> O
VI.	0.25 Na <sub>2</sub> O	19.118	8.1	—	34.3	8.86	4.1 Na <sub>2</sub> O
VII.	0.21 K <sub>2</sub> O	19.072	5.4	26.69	—	4.54	3.15 K <sub>2</sub> O
VIII.	0.21 Na <sub>2</sub> O	19.257	5.9	—	11.5	2.97	1.9 Na <sub>2</sub> O
IX.	0.17 K <sub>2</sub> O	19.125	3.5	5.99	—	1.02	1.1 K <sub>2</sub> O
X.	0.17 Na <sub>2</sub> O	19.381	3.2	—	4.19	1.08	1.27 Na <sub>2</sub> O

The two water-glasses had only been so far dissolved as is shown in the table. After cooling, the powdered water-glass was found to have become a coherent amorphous mass, which, in the case of the potash glass, appeared homogeneous, but, in the case of the soda glass, full of grains. Of the other glasses, the only one that exhibited this coherence was No. III.; all the others retained the condition of completely separated grains.

The table shows, as was to be expected, that the solubility of both potash and soda glass diminishes rapidly as the content of lime increases. In the comparison of the potash with the soda glasses, the most prominent fact is the superior resisting power of the soda glasses. The superiority however diminishes as the



content of lime increases. The following are the total amounts of dissolved matter, including both silicic acid and alkali :

Content of Lime.	Dissolved matter in mg.		
	Soda Glass.	Potash Glass.	Ratio.
$\frac{1}{4}$ Molecule	506.7	4673	1 : 9.2
$\frac{1}{2}$ "	42.4	223.5	1 : 5.3
$\frac{3}{4}$ "	17.4	32.1	1 : 1.8
1 "	7.4	9.5	1 : 1.3

The following is a list of the amounts of oxygen in the dissolved alkalis, or of 16 times the number of milligram-molecules of alkali dissolved :

Content of Lime.	Alkali-oxygen in mg.		
	Soda Glass.	Potash Glass.	Ratio.
$\frac{1}{4}$ Molecule	52.33	285.2	1 : 5.5
$\frac{1}{2}$ "	8.86	26.9	1 : 3.3
$\frac{3}{4}$ "	2.97	4.54	1 : 1.5
1 "	1.0	1.0	1 : 1.0

Lastly, the ratio of alkali to silicic acid in the solution is worthy of attention. The solution contains, in every case, relatively more alkali than the glass. In our table of direct results, the second column gives the ratio of alkali to silicic acid in the glass, and the last column gives the corresponding ratio in the solution, which is in every case greater than in the glass. The ratio of the numbers in the two columns is exhibited in the following list :

Content of Lime.	Soda Glass.	Potash Glass.
None	1 : 1.14	1 : 1.08
$\frac{1}{4}$ Molecule	1 : 2.19	1 : 1.23
$\frac{1}{2}$ "	1 : 16.4	1 : 6.24
$\frac{3}{4}$ "	1 : 9.12	1 : 15.12
1 "	1 : 7.62	1 : 6.6

In the case of each of the two kinds of glass, there is a certain content of lime which gives a maximum of inequality to the ratio, and this proportion of lime is larger for potash than for soda glass. Mylius and Foerster arrive at the conclusion that, in good glasses, double silicates of lime and alkali, in mutual connection, promote resisting power against water.

**135. Comparison of Commercial Glasses.**<sup>1</sup> The method of testing described in the preceding article has been applied, in altered form, by Mylius and Foerster, to 11 different commercial glasses. The following table gives, in weights per cent., those components which are important for our purpose:

No.	Description.	SiO <sub>2</sub> .	Na <sub>2</sub> O.	K <sub>2</sub> O.	CaO.	PbO.
1	Yellow alkaline glass - -	60.49	15.41	13.25	5.42	—
2	Inferior Thuringian - -	69.92	16.5	6.6	3.75	—
3	Glass of Tittel & Co. - -	71.5	14.3	7.1	6.7	—
4	Schilling's flask glass - -	75.2	11.9	4.2	8.3	—
5	Kavalier Bohemian - -	78.3	1.4	13.3	6.8	—
6	Rhenish window-glass - -	71.2	13.5	—	13.4	—
7	Lead crystal; Ehrenfeld - -	56.0	0.6	12.1	—	31.2
8	Green flask; Charlottenb. - -	63.5	9.5	1.3	14.0	—
9	Jena thermometer 16 <sup>III</sup> - -	67.5	14.0	—	7.0	—
10	Jena lead glass 483 - -	44.75	0.2	7.3	—	47.0
11	Lead silicate - - -	21.7	—	—	—	78.3

No. 1 contained 0.22 per cent. of sulphur, and was coloured yellow by sulphur-alkali. No. 8 contained 3.9 per cent. of magnesia. The normal-thermometer glass contains zinc oxide 7 per cent., and boric acid 2 per cent.

The results are given in the following resumé, which is an extract from Mylius and Foerster's table.<sup>2</sup> They are arranged in the same form as the direct results given in last article, except that one column is omitted. The numbers in the last column now include, of course, both alkalis, when both are present in the glass. The glasses are arranged in the order of their total losses by the five hours' immersion in hot water.

<sup>1</sup> M. u. F., I. and II.

<sup>2</sup> M. u. F., I. 1107.

No.	Quantity gm.	In 60 c.c. of solution.				
		SiO <sub>2</sub> mg.	K <sub>2</sub> O mg.	Na <sub>2</sub> O mg.	Oxygen in Alk. mg.	Molec. Alk. to 1 SiO <sub>2</sub> .
1	19.451	84.7	59.0	98.5	35.6	1.5
2	19.125	14.3	18.1	59.0	18.4	4.8
3	19.304	6.9	6.5	14.4	4.8	2.7
4	19.079	5.3	1.7	4.8	1.5	1.1
5	18.468	5.5	5.3	—	0.8	0.6
6	18.963	4.3	—	4.6	1.2	1.0
7	23.543	1.9	7.0	—	1.2	2.3
8	20.162	3.2	—	2.7	0.7	0.9
9	20.000	2.7	—	3.2	0.8	1.2
10	27.814	1.5	1.8	—	0.3	—
11	49.021	0.6	—	—	—	—

In cold water, the removal of soluble matters from the glasses is a very slow process, and is found—by the iod-eosin colour test<sup>1</sup>—to give a somewhat different order of arrangement from the above. For example, Kavalier's Bohemian glass is less affected than normal-thermometer glass, although much more affected by hot water. Mylius and Foerster's explanation is, that the lime and zinc oxide in the thermometer glass bind the soda, while in the Bohemian glass the quantity of lime is not sufficient to do this. They allude to the fact that water-glass is at first almost unaffected by cold water, but offers little resistance to hot.

The first action of cold water on glass consists mainly in the removal of alkali. The alkaline solution thus formed takes up silicic acid with increasing rapidity, and the more so the higher the temperature is. Mylius and Foerster infer that the susceptibility of glasses to attack by cold water can be approximately estimated by the number of milligram-equivalents of alkalis removed by hot water, or by the amount of oxygen contained in the alkalis in the solution. This gives, for the above 11 glasses, the order 1, 2, 3, 4, 6, 7, 9, 5, 8, 10, 11.

The last column in the table of results shows that, in nearly all cases, the solution contains more molecules of alkali than of silicic acid.

<sup>1</sup> Art. 132.

Besides silicic acid, potash, and soda, the solution also contained lime, and zinc or lead, but only in traces too small to admit of an estimate. The lime certainly goes into solution as hydrate; and in like manner baryta glasses give baryta hydrate.

**136. Quantitative Analysis of the Material Dissolved from Glass by Cold Water.** The first quantitative determination of the substances taken out of glass by cold water seems to have been made by F. Kohlrausch.<sup>1</sup> It applied to two glasses—a chemical glass rich in alkali, and a Bohemian glass rich in silica. The following are their compositions in equivalents per cent.; the molecular weights of the glass-forming oxides being reckoned as their equivalents:

	SiO <sub>2</sub> .	Na <sub>2</sub> O.	K <sub>2</sub> O.	CaO.	Al <sub>2</sub> O <sub>3</sub> .
Chemical glass,	72	20·3	1·3	4·0	2·1
			SiO <sub>2</sub> .	Alkali.	CaO.
Bohemian glass, -	-	-	82	10·3	7·9

The ratio of potash to soda in the Bohemian glass was 6·3 to 1; but an exact separation of the two metals in the solution formed from it was impracticable. In the calculation of the analysis they were assumed to have the same ratio as in the glass.

Nine gm. of the chemical glass, reduced to powder, were treated with 250 gm. of water; and 220 gm. of the clear solution which was poured off gave 124 mg. of dry material. The solution therefore contained 560 mg. per litre.

The analysis was effected with the aid of hydrochloric acid, ammonia, ammonium oxalate, silver nitrate, and platino-hydrochloric acid; and gave, in equivalents per cent.:

	SiO <sub>2</sub> .	Na <sub>2</sub> O.	K <sub>2</sub> O.	CaO.	Al <sub>2</sub> O <sub>3</sub> .
Chemical glass,	40	57	0·8	0·2	2·0

Thus, for one molecule of silicic acid, the glass contained 0·3 molecule of alkali, and the solution 1·44.

Eight gm. of the Bohemian glass, in the state of powder, were left for six weeks in contact with 200 gm. of water at 8°. The solution, after two filterings, contained 61·5 mg. of dry material

<sup>1</sup> K., III.



in 143 c.c., which is at the rate of 430 mg. per litre. The analysis gave, in equivalents per cent.:

	SiO <sub>2</sub> .	Alkali.	CaO.
Bohemian glass,	76	18	6

For one molecule of silicic acid, the glass contained 0.13 molecule of alkali, and the solution 0.24.

It is also to be noted that sensible quantities of alumina from the chemical glass, and of lime from the Bohemian glass, went into solution.

### 137. Titration and Colour Tests with Iod-eosin and Ether.<sup>1</sup>

As the dissolving of alkalis plays a leading part in the decomposition of glass by water, Mylius and Foerster proposed that the susceptibility of glass to the action of water should be determined by measuring the quantity of alkali in the solution. This proposal led to a search for sensitive methods of measuring small quantities of alkali; and by the employment of iod-eosin (which had previously been used by Mylius in comparative tests), two suitable methods were worked out.

**Titration, with Millinormal Solutions.** In the determination of fairly large quantities of alkali by normal or decinormal solutions, there is no reason for departing from the regular practice. Determinations with centinormal solutions can also be carried out with some degree of certainty in the ordinary way; but this is about the limit.

With the help of iod-eosin and ether, determinations can however be made with millinormal solutions of sulphuric acid, and with increased sharpness. In preparing these solutions, great attention must be paid to the necessity of employing pure (or at least neutralised) water, as the alkaline impurities communicated to distilled water by the glass vessels in which it has been kept, will produce disturbance. Millinormal solutions may be kept for some time in vessels of *good* glass.

The alkaline solution to be tested is put into a stoppered bottle, and covered with a layer of very dilute eosin solution. Small quantities of the acid solution are then added, with vigorous shaking, until the watery layer, which was originally red, just

<sup>1</sup> M. und F., III. and IV.

loses its colour. Each c.c. of acid solution corresponds to .031 mg. of soda ( $\text{Na}_2\text{O}$ ) or .047 mg. of potash ( $\text{K}_2\text{O}$ ).

**Measurement of Alkali by Colour Test.** This method of titration suffices for detecting and measuring in 100 c.c. of water a quantity of alkali equivalent to 0.1 mg. of soda ( $\text{Na}_2\text{O}$ ). For smaller quantities of alkali than this, the process is not applicable, and the following colour test is to be preferred.

If a very dilute aqueous solution of alkali is shaken up with an etheric solution of eosin, containing an excess of iod-eosin above what is necessary for neutralising the alkaline solution, eosin-alkali is formed, and the mixture acquires a rose colour, of intensity proportional to the quantity of alkali remaining unneutralised. In determining the amount of alkali by this colour test, certain precautions are to be observed, for which, as well as for a full account of the titration method, we must refer to M. u. F., III. Iod-eosin is affected by soda, potash, lime, and any other alkaline components of the glass that may be given off to the water. The result depends merely on the total number of equivalents of alkali, without regard to kind, and is usually stated in terms of the quantity of soda that would be equivalent to all the alkali given off.

**138. Earliest Employment of the Quantitive Test by Iod-eosin.**<sup>1</sup> In working out the methods of testing briefly described in last article, Mylius and Foerster had immediately in view the selection of the best glasses for chemical uses from among the various kinds in the German market. For this purpose, flasks and bottles by the most eminent makers were obtained from the authorities at the Reichsanstalt, who were asked to furnish the best kinds available, and to state their origin. The capacities of the vessels were from 250 c.c. to 300 c.c. The flasks were spherical, and the bottles cylindrical, so that the wetted areas could be determined with close approximation.

**Preliminary Trials.** To find out the best way of testing, the following preliminary experiments were made, upon the action of water on glass surfaces under various external conditions.

A. The flasks and bottles were freed from adherent products of weathering by repeated rinsing with water,<sup>2</sup> and then left for

<sup>1</sup> M. u. F., IV. 315.

<sup>2</sup> Here, and in what follows, *neutral* water is to be understood.

24 hours in contact with water at 20°. The alkalinity of the water was then determined, either by titration or by colour estimation. The numerical values in the table below denote the quantity of alkali given off from each square decimeter of glass surface to the water, expressed in thousandths of a milligram of soda, as above explained.

No.	Flasks.	Alkali.
1.	Kähler & Martini, - - - -	5
2.	Schweig & Co., Weisswasser, - -	10
3.	Kavalier, Sazava, Bohemia, - -	12
4.	Bohemian Hollowglass, - - -	14
5.	Fettke & Ziegler, Doebern, - - -	25
6.	Leybolds Nachf., Cologne, - - -	53
7.	Bohemian Glass, - - - -	66
8.	Warmbrunn, Quilitz & Co., - - -	66
9.	Schilling, Gehlberg, - - - -	83
10.	Tritschler & Co., Stuttgart, - - -	309
11.	Lambach, Bavarian Forest, - - -	435

No.	Bottles.	Alkali.
I.	Bohemian Hollowglass, - - -	23
II.	Warmbrunn, Quilitz & Co., - - -	30
III.	Fettke & Ziegler, Doebern, - - -	31
IV.	Schilling, Gehlberg, - - - -	42
V.	Kähler & Martini, - - - -	76
VI.	Leonhardi, Schweppnitz, - - -	189
VII.	Stender, Lampspringe, - - -	201
VIII.	Schweppnitz Works, - - - -	339
IX.	Leybolds Nachf., Cologne, - - -	498

The initial intensity of action, as measured by these numbers, depends entirely on the weathering and other changes which the surface may have previously undergone.

*B.* The bottles were subjected on the second, third, and fourth day to the same treatment as on the first. They were then left, for a week at a time, for three weeks in succession, and the average amount of alkali taken up per day was deduced. The

following were the daily amounts thus found (in the same units as above).

Bottle.	1st day.	2nd day.	4th day.	5th to 11th. Mean.	12th to 18th. Mean.	19th to 25th. Mean.
I.	23	2.9	3.0	2.0	0.66	—
II.	30	6.7	4.5	1.5	0.8	0.25
III.	31	6.8	4.4	2.6	1.4	0.5
IV.	42	16	11	8.0	5.2	2.8
V.	76	28	21	15	10.9	5.3
VI.	189	53	16	9	6.2	3.1
VII.	202	65	20	11	8.8	4.5
VIII.	340	101	16	9	6.9	3.9
IX.	499	111	53	28	22.7	12.6

A glance at this table shows that the amount of alkali given to the water on the first day is much greater than on the following days; and the order of the glasses, as regards amount of action, does not remain the same throughout the trial.

It is not necessary to suppose that the outermost layer of the surface is specially rich in alkali. The water has direct access to the first layer, but cannot attack the others without getting through a very impermeable shield of silica and silicate of lime.

C. Bottles of the same origin as the above were then left for an hour, with water at  $80^{\circ}$  in them, and then quickly cooled. This was done several times in succession, the water being renewed each time, and the alkali in the previous filling measured. We do not reproduce the results, as they were unsatisfactory.

Another trial on the same lines was then made with three flasks, of glasses differing very widely from one another; and special attention was paid to the maintenance of one uniform temperature. The following were the results thus obtained:

Flask.	1st.	2nd.	3rd.	4th.	5th.	6th.	7th.	8th.	9th.	10th.
2	23	4.4	4.4	4.4	4.2	4.4	3.8	2.9	3.8	3.8
6	137	52	31	25	19	18	17	15	16	16
9	360	129	94	75	69	60	55	54	52	—



The quantity of alkali dissolved in the first hour is here greater than in 24 hours with cold water. The rate of dissolving attains its permanent value earlier with good glass than with bad.

*D.* From the above experiments it would appear that glass bottles tend to improve with continued use. Specially good glasses, after some time, cease to give off alkali to any appreciable extent; but glasses of moderate quality will continue to render distilled water alkaline even after the lapse of years.

Warburg and Ihmori have accordingly suggested that glass vessels should be kept full of boiling water for long periods, in order to improve them by the removal of alkali from their surfaces; and trials have been made to ascertain how far this mode of improvement is practicable. The upshot of the trials was, that in glasses of poor quality, intended for holding cold water, a preliminary treatment with hot water is very beneficial. The absorption of alkali will not however be thus altogether stopped. Even 100 hours of contact with boiling water will not suffice to prevent a bad glass from being decomposed by cold water.

*E.* When glass has been strongly attacked by hot water, as in the experiments above recorded, the contrast between good and bad glass becomes much less marked. This is shown by further experiments which were made on the three flasks above mentioned. After their 10 hours of exposure to water at  $80^{\circ}$ , as described in *C*, they were continuously subjected for 6 hours, in a bath of boiling water, to the action of pure water obtained by distillation in an apparatus of platinum. Under this treatment, the amounts of alkali which they gave up to the water from each sq. decim. of wetted surface, were (in mg. of  $\text{Na}_2\text{O}$ ), 0.89 from No. 2, 1.51 from No. 6, 2.50 from No. 9.

These are as  $1 : 1.8 : 2.8$ ,

whereas for the first hour (see table in *C*) the quantities were as

$1 : 6 : 15.7$ ,

and for the ninth hour as  $1 : 4.2 : 13.7$ .

The total quantities of matter dissolved in the six-hour experiment were determined, by evaporating the solutions; and

were not excessively different for the three flasks, the extreme values being about four and about six mg. per sq. decim.

*F.* In order to obtain trustworthy comparisons of the susceptibilities of different glasses to attack by water, great care must be taken to ensure constancy of temperature. Mylius and Foerster illustrated this point by operating in identical fashion on four equal flasks (by Greiner & Co.) with water at 0°, 18°, 40° and 80° respectively. The amounts of alkali dissolved, expressed in thousandths of a milligram of soda per sq. decim., were :

In 24 hours, at	0°	-	-	-	1.9
"	"	18	-	-	6.4
In 1 hour,	42	-	-	-	9.1
"	"	80	-	-	153

**Practical Testing of Glass Vessels.** The complete testing of a specimen of glass, as regards its behaviour towards water, is a complex business, as the above investigations show. The practical requirements for a ready and sensitive method of determining the relative merits of glass vessels from different sources, are fairly satisfied by exposing the vessels (as yet unused) to the action of water, and comparing the quantities of alkali dissolved. Any disproportion which may exist between the silica and alkali dissolved is left out of account. On these lines, Mylius and Foerster have carried out the following comparisons.

The vessels were first exposed for three days to the contact of water at 20°, and the solution thus obtained (which of course included products of weathering) was put aside. The vessels were then exposed for another three days to contact with a fresh supply of pure water; and these second solutions were tested by iod-eosin and ether, for the quantities of alkali which they contained. The quantity of alkali per unit of wetted surface, was taken as the measure of susceptibility to attack by cold water.

The following results were obtained by carrying out this programme, except that, during the preliminary three days' exposure, the water was changed on the second day. Also, at the conclusion of the test with cold water, which occupied the second three days, a one-hour test was made with hot water at 80° :

Glass.		20°	80°
Kähler & Martini, - -	Flasks	1.0	6.7
Schweig & Co., - - -	,,	1.5	8.9
Kavalier, - - - -	,,	2.1	8.9
Fettke & Ziegler, - -	,,	3.7	29
Normal-thermometer 16 <sup>III</sup> , -	,,	4.0	43
Bohemian hollowglass, -	Bottles	10	43
Bohemian hollowglass, -	Flasks	7.2	78
Warmbrunn, Quilitz & Co.,	Bottles	8.9	81
Fettke & Ziegler, - -	,,	7.6	107
Leybolds Nachf., - -	Flasks	13	176
Lambach Works, - -	,,	13	203
Warmbrunn, Quilitz & Co.,	,,	17	211
Bohemian glass, - - -	,,	21	200
Schilling, - - - -	,,	26	270
Schilling, - - - -	Bottles	21	341
Stender, - - - -	,,	41	279
Leonhardi, - - - -	,,	41	378
Schweppnitz Works, - -	,,	50	331
Kähler & Martini, - -	,,	51	405
Tritschler & Co., - - -	Flasks	40	558
Leybolds Nachf., - -	Bottles	100	472

The unit is  $\frac{1}{1000}$  of a milligram of soda per square decimetre.

The numbers show that most of these glasses are fit for the ordinary work of chemical laboratories, but that only a few satisfy the more stringent requirements.

**Chemical Composition of Six of the Glasses.** Mylius and Foerster came to the conclusion that, of the flasks, the best are those of Kähler & Martini, of Schweig & Co., and of Kavalier; and of the bottles those of Bohemian hollowglass. Of these they give the following analysis, together with those of flasks 6 and 9, which, together with 2, were subjected to the experiments

No.		SiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub>
1.	Kähler & Martini, -	75.4	9.3	4.4	9.9	1.0
2.	Schweig & Co., - -	78.8	10.1	3.6	7.2	0.3
3.	Kavalier, - - -	79.1	6.4	6.7	7.6	0.2
1.	Bohemian hollowglass,	76.5	9.2	5.5	8.2	0.6
6.	Laybolds Nachf., -	76.5	10.4	6.6	5.9	0.6
9.	Schilling, - - -	73.1	13.4	5.3	5.8	2.2

described in *E*. The values are percentages by weight. The last glass contained also 0.2 per cent. of MnO.

There is a general opinion among glassmakers that glass containing one molecule of alkali and one of lime for every six of  $\text{SiO}_2$  is specially resisting against chemical attack. Mylius and Foerster give, as a test of the correctness of this view, the following values for the first four glasses in the above list, and also for the glass employed by Stas for the vessels used in his determinations of atomic weights.

	For every 6 molecules of $\text{SiO}_2$ .				
	Kahl.	Schweig	Kav.	Bohem.	Stas.
Mol. Alkali	0.95	0.90	0.72	0.99	0.76
Mol. CaO	0.85	0.60	0.57	0.69	0.86

The percentage composition of the Stas glass is 77  $\text{SiO}_2$ , 5  $\text{Na}_2\text{O}$ , 7.7  $\text{K}_2\text{O}$ , 10.3 CaO.

**139. Later Rules for Times of Exposure.** Later researches have shown that the preliminary three-day treatment with water at  $20^\circ$  completely suffices to remove all products of weathering from the surface of the glass. They have shown, at the same time, that to obtain certain results, great care must be taken to preserve constancy of temperature; and further, that to find the quantities of alkali given up by good glasses, the exposure to cold water (at  $20^\circ$ ) must be extended to a week, and the treatment with hot water to three hours.

Foerster (see F., V.) has followed these rules in obtaining further comparisons of some of the glasses indicated as best in his previous iod-eosin tests, with one another, and with some additional glasses.

The total number of glasses was 14, and they had the following compositions.

Glasses 1-11 were known to have great power of resisting attack.

15 and 16 are commercial glasses easily attacked.

17 is a good lead crystal glass.

1, 2, 10 are Jena glasses, 1 being borosilicate, and 10 normal-thermometer glass.

In addition to the components mentioned in the table, No. 1 had 12 per cent.  $\text{B}_2\text{O}_3$ ; No. 2 had 5 per cent.  $\text{ZnO}$ ; No. 10 had 7 per



cent. ZnO, and 2 per cent.  $B_2O_3$ ; No. 17 had 30 per cent. PbO. There were small quantities of MnO, which are left out of account.

No.	SiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	Alkali.
1=59 <sup>III</sup>	71.9	11.0	—	—	5.0	10.8
2=165 <sup>III</sup>	74.4	9.8	—	7.0	3.5	10.0
3	75.9	7.6	5.8	10.4	0.3	11.2
4	76.6	6.7	6.6	9.5	0.6	11.0
5	76.8	6.4	6.2	10.0	0.4	10.4
6	76.3	8.3	7.0	8.1	0.3	12.7
7	75.1	4.9	11.8	7.6	0.5	12.8
8	77.6	10.0	4.3	7.8	0.3	12.6
9	77.2	10.1	4.6	7.7	0.4	13.0
10=16 <sup>III</sup>	67.5	14.0	—	7.0	2.5	14.0
11	70.6	14.3	0.6	11.2	2.9	14.6
15	74.1	9.0	9.7	6.8	0.4	15.4
16	68.9	13.7	6.7	7.2	3.2	18.6
17	57.3	—	12.7	—	—	11.0

The last column gives the number of molecules of alkali to every 100 molecules of glass-forming oxides.

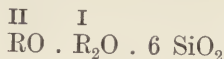
The tests were applied to flasks made of the glasses. In the following summary of results, the unit is, as before, the thousandth of a milligram of soda per sq. decim. The last column gives the ratio of the numbers in the two preceding columns:

No.	Alkali taken up.		Ratio.
	8 days at 20°	3 hours at 80°	
1= 59 <sup>III</sup>	2.5	2.7	1.1
2=165 <sup>III</sup>	2.1	6.3	3.0
3	10.7	28.4	2.65
4	8.9	28.2	3.17
5	13.1	26.8	2.05
6	14.0	56	4.00
7	14.5	45	3.10
8	14.9	50	3.40
9	17.8	66	3.72
10= 16 <sup>III</sup>	16.6	65	3.91
11	27	98	3.63
15	32	217	6.78
16	77	654	8.5
17	74	350	4.73

The two glasses at the head of the list show very much greater resisting power against both cold and hot water than any of the others. In the case of the 59<sup>III</sup> Foerster attributes this to the large content of acid oxides; silicic and boric acid make up 84 per cent. of its composition.

The following conclusions (to the end of this article) are also drawn by Foerster.

In glasses 3 to 9, and 11, all of them ranking as specimens of the best commercial glasses for chemical use, the number of molecules of alkali per 100 molecules of glass-forming oxides, is a material element in their resisting power against water. The current opinion among glass-makers that the ideal type of a glass of good resisting power is an approximation to



is not supported by the comparison of 8 with 11; for 11 comes much nearer to this so-called normal formula than 8, and yet is much more attacked.

The view insisted on by R. Weber<sup>1</sup> some time ago as to the importance of a proper ratio of lime to alkali and silica finds little support till we come to the comparison of 11 with 15.

Glasses 7 and 8 furnish a further illustration of the remark that in good glasses it is immaterial whether potash or soda predominates.

A comparison of 8 with 9 seems to show that a trifling increase in the proportion of alkali may produce a large diminution of resisting power.

The difference between the effects of hot and cold water varies considerably. In the inferior glasses it increases as we go from better glasses to worse. In the lead crystal it is rather small, owing perhaps to the presence of a layer of hydrated lead silicate, which hinders penetration.

When resistance to cold water only is in question, as in the finest spirit-levels, one of the first 8 glasses should be employed.

Attention is called to the announcement that, as a consequence of the stimulus furnished by the labours of the Reichsanstalt, vessels of the glass used by Stas are now commercially obtainable.<sup>2</sup>

<sup>1</sup> *Ann. d. Phys. u. Chem.*, 6, 431 (1879).

<sup>2</sup> *Chem. Repert. Suppl. z. Chem.*, 16, 257.

**140. Tests with Water Above the Normal Boiling Point.**

The action of water heated under high pressure comes into consideration, in the case of gauge tubes for steam boilers, and for some of the uses of the chemical laboratory.

Researches specially directed to this subject were published by Foerster in 1892.<sup>1</sup> Glass tubes three-quarters filled with distilled water, the remainder being occupied by air, were sealed, and then immersed upright for six hours in boiling aniline (temp. 183°). When the glass came to be examined, the surface was found to be sharply divided into two parts at the line of demarcation between water and steam.

The part exposed to the steam had become coated with an opaque white layer of products of decomposition. This layer could be rubbed off, and, after drying in air, readily gave off alkali and silica to cold water.

The part which had been in contact with the water was covered with a white flocky material, easily removed, portions of which had become detached and were swimming in the water. They consisted mainly of silica with a little lime. The quantity of alkali which had gone into solution was so considerable that, even in the case of the best tubes in use up to that date, it could be measured by titration with a decinormal solution. Considerable quantities of silica were also dissolved. An analysis, which was made in one case, showed that the water had soaked in, just as was previously found with more moderate temperatures.

Four glasses were heated for six hours in water at 183°, and tested for dissolved alkali by titration with decinormal solutions, very dilute iod-eosin being employed as indicator. The following results are given by Foerster as the means of several trials. The alkali is reduced as usual to its equivalent in soda, and expressed in mg. per sq. decim.:

A. Ordinary gauge-tube glass,	-	-	-	22.4
B. Better quality,	-	-	-	13.7
C. Kavaliers combustion-tube glass,	-	-	-	7.1
D. Jena compound glass,	-	-	-	1.1

The inner surface of the tubes of compound glass (see Art. 101), is the borosilicate 59<sup>III</sup>, which, whether alone or as one of the layers of a compound glass, is more proof against attack by super-

<sup>1</sup> F., I. 2494-2497.

heated water than the other glasses experimented on, one of which, C, had up to that time been regarded as the most resisting of all gauge-tube glasses. The borosilicate, when subjected to the test above described, was not corroded either by the water or by the steam, but remained—unlike all the other glasses—perfectly smooth and transparent.

Foerster subsequently<sup>1</sup> carried out more elaborate and exact tests with ten glasses, which we designate 1, 4, 7, 9, 10, 11, 12, 13, 14, 16. So far as these numbers agree with those in the preceding articles, they denote the same glasses. The following are their compositions, in weights per cent.:

No.	SiO <sub>2</sub> .	Na <sub>2</sub> O.	K <sub>2</sub> O.	CaO.	Al <sub>2</sub> O <sub>3</sub> .	Alkali.
1=59 <sup>III</sup>	71.9	11.0	—	—	5.0	10.8
4	76.6	6.7	6.6	9.5	0.6	11.0
7	75.1	4.9	11.8	7.6	0.5	12.8
9	77.2	10.1	4.6	7.7	0.4	13.0
10=16 <sup>III</sup>	67.5	14.0	—	7.0	2.5	14.0
11	70.6	14.3	0.6	11.2	2.9	14.6
12*	78.9	1.0	14.0	5.8	0.2	10.4
13*	73.0	12.9	1.8	11.0	1.3	13.8
14*	—	—	—	—	—	—
16	68.9	13.7	6.7	7.2	3.2	18.6

In addition to the components here specified, No. 1 contained B<sub>2</sub>O<sub>3</sub>, 12 per cent.; No. 10, ZnO, 7 per cent., and B<sub>2</sub>O<sub>3</sub>, 2 per cent. The composition of No. 14 is not stated. The content of MnO (which is given in F., V.) is neglected.

The three numbers with asterisks belong to gauge-tube glasses in practical use, and the first two were described as specially good. The column headed "alkali" gives, as before, the number of molecules of alkali in every 100 molecules of glass-forming oxides.

The following was the method of testing. Portions of tubes of the different glasses were dried at 100°, and weighed. They were then enclosed with water in carefully cleaned iron tubes, and heated for 4 hours at 190°. These tubes having been cooled down and opened, the alkali taken up by the water was determined in equivalents of soda, by titration with centinormal and deci-

<sup>1</sup> F., V.



normal solutions; and at the same time the bits of glass tube, having been freed from loosely adhering products of decomposition, were dried at  $500^{\circ}$ – $550^{\circ}$ , and then weighed to ascertain their losses. These losses are given in the second column of the following table, in mg. per sq. dec. of glass surface. In the case of glass 11, the agreement between single observations was not close enough to give a trustworthy mean. The quantities of alkali taken up by the water, expressed by their equivalents in soda, are given in the fourth column. From these, the actual quantities of alkali given in the third column are calculated, on the assumption that the ratio of potash to soda is the same in the solution as in the original glass, the small quantity of dissolved lime being neglected. These quantities of alkali, subtracted from the totals in the second column, leave remainders representing the amounts of silica dissolved. The last column of the table gives the number of molecules of  $\text{SiO}_2$  to one molecule of alkali, as calculated from these remainders.

No.	Loss in mg. per sq. dec.			Molecules of $\text{SiO}_2$ .
	Total.	Alkalis.	Equiv. in $\text{Na}_2\text{O}$ .	
1=59 <sup>III</sup>	23.7	3.5	3.5	6.0
4	17.2	5.6	4.6	2.65
7	51.3	15.4	11.1	3.35
9	67	16.4	14.7	3.57
10=16 <sup>III</sup>	34	6.4	6.4	4.42
11	?	7.3	7.3	
12*	63	16.2	10.7	4.5
13*	37	8.3	8.3	3.6
14*	87	—	29	—
16	126	61	52	1.3

The order of the glasses as determined by the amounts of alkali dissolved at  $190^{\circ}$  is different from the order at  $20^{\circ}$ , and from the order at  $80^{\circ}$ . Foerster maintains that the glasses which are rich in lime and zinc, and approximate in their composition to the so-called normal formula,



are much more resisting than glasses poor in lime and rich in silica, which approximate to the composition of water-glass. In

correspondence with their greater solubility, glasses of the latter kind take in considerable quantities of water at  $190^{\circ}$ , which produce flaking off when the glass is subsequently heated—a phenomenon not exhibited by glasses 4, 10, 11, 13, which are rich in lime and zinc.

The quantities of silica taken up by the water at  $190^{\circ}$  are so large, in comparison with the dissolved alkali, that they cannot be left out of account in estimating the goodness of the tubes.

Judged by the quantity of dissolved alkali, the borosilicate 59<sup>III</sup> is the most resisting of all the glasses in the table. Judged by the quantity of dissolved silica, it is inferior to No. 4, and to no other. It has an advantage over all the other gauge-tube glasses in retaining its transparency when exposed to highly superheated water. Not till the temperature exceeds  $250^{\circ}$  is its surface corroded by water or steam. Of the other glasses, those which are most strongly resisting, having a large content of lime, are specially subject to obscuration of surface, owing to a deposit of silicate of lime. It may also be mentioned that tubes of 59<sup>III</sup> have remained in good preservation when they have been employed for containing neutral substances, with water at high temperatures.

**141. Weathering of Glass Surfaces.** The durability of a glass in moist air depends mainly upon its resisting power against attack by water. Bunsen has shown<sup>1</sup> that dry carbonic acid exerts no action of any kind upon glass quite free from water.

It must be assumed that hygroscopic glasses begin by taking water into chemical combination with their surface layer, whence arises the swelling up of the surface, observed by Foerster (Art. 133). As a result of this absorption of water, alkaline components of the glass are gradually set free, and these afford the first opportunity for the action of the carbonic acid of the air.

Experiments on the susceptibility of glass to attack by cold water give accordingly a measure of its susceptibility to weathering.<sup>2</sup>

The carbonic acid of the air combines with these alkalis from the glass to form the carbonates  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ , which, on drying, are deposited in the form of crystals. They can easily be removed by rinsing with water. Mylius and Foerster have shown that the quantity of carbonate thus formed may be very

<sup>1</sup> *Ann. d. Phys. u. Chem.*, 24, 321 (1885).

<sup>2</sup> *F.*, II. 2919.

considerable.<sup>1</sup> The experiments which they made with eleven flasks do not, however, furnish a satisfactory basis for determining the susceptibilities of the glasses to weathering, as too little was known respecting their previous history.

#### 142. Testing by Electrical Conductivity of the Solution.

A very simple and comparatively exact measure of the susceptibility of glass to attack by water is furnished by the electric conductivity of the solution formed by the attack. This test was first systematically applied by F. Kohlrausch.<sup>2</sup>

Observation of the conductivity of the solution establishes, as a universal proposition, that glass does not, like the majority of very insoluble substances, pass over unchanged into the solution but is gradually decomposed. Such bodies as gypsum, calcspar, fluorspar, heavyspar, and chloride of silver, when left in contact with water, give a solution which, if its temperature is kept constant, soon attains a permanent conductivity. With glasses, on the contrary, no limit to solubility is attained. In observations extending over weeks or months, the quantity of matter in solution continues to increase, though at a diminishing rate. The conductivity test affords great facility for tracing the gradual progress of chemical action.

**The Kinds of Glass Tested.** Kohlrausch's first comprehensive examination included thirty-one kinds of glass. In addition to chemical bottle glasses procured by himself, there were tube glasses, supplied to him by the Reichsanstalt, and a collection of glasses, chiefly optical, from the Jena works. The chemical compositions of the Jena glasses were furnished by the senders. The compositions of the tube glasses were supplied by the Reichsanstalt. Several of these glasses had already been tested, by iod-eosin or by direct analysis, for their behaviour to cold or hot water. The bottle glasses were analysed, some of them at the Reichsanstalt, and some at the Jena works.

From these data, Kohlrausch calculated the following table of equivalents per cent. for all the glasses, except Nos. 2 and 3, which were not analysed. In making the calculations, he employed, as the molecular weights of the several glass-forming oxides, the numbers which stand at the head of the table, immediately under the chemical symbols for these oxides.

<sup>1</sup> M. u. F., IV. 323.

<sup>2</sup> K., I. and II.

## COMPOSITION IN EQUIVALENTS PER CENT.

No.	SiO <sub>2</sub> 60	Na <sub>2</sub> O 62	K <sub>2</sub> O 94	CaO 56	Al <sub>2</sub> O <sub>3</sub> 102	MgO 40	PbO 223	ZnO 81	MnO 70	BaO 153	As <sub>2</sub> O <sub>3</sub> 198	B <sub>2</sub> O <sub>3</sub> 70	P <sub>2</sub> O <sub>5</sub> 142
1	67.6	16.3	3.52	10.0	2.29	—	—	—	0.17	—	—	—	—
4	77.0	9.7	3.64	9.2	0.44	—	—	—	—	—	—	—	—
5	72.1	20.3	1.31	3.96	2.11	—	—	—	0.25	—	—	—	—
6	76.2	4.85	11.1	2.99	—	—	—	—	0.09	—	—	—	—
7	69.0	14.5	—	7.74	1.52	—	—	5.35	0.18	—	—	1.77	—
8	78.0	5.66	6.61	—	—	—	9.55	—	0.08	—	0.08	—	—
9	50.9	—	—	—	—	—	49.0	—	0.01	—	0.07	—	—
10	73.6	5.1	10.1	9.62	—	—	—	—	0.09	—	0.06	1.36	—
11	76.2	11.6	2.75	9.03	0.40	—	—	—	trace	—	—	—	—
12	81.8	1.41	8.87	7.61	0.31	—	—	—	—	—	—	—	—
13	68.2	13.9	4.53	10.9	2.18	—	—	—	0.3	—	—	—	—
14	70.8	8.23	9.49	7.97	—	—	—	2.36	0.09	—	0.10	0.91	—
15	73.1	14.2	4.63	7.33	0.24	0.31	—	—	0.18	—	—	—	—
16	68.8	14.1	4.0	11.2	1.7	—	—	—	0.2	—	—	—	—
17	70.6	15.9	3.9	8.1	1.1	—	—	—	0.4	—	—	—	—
18	72.1	17.5	3.9	4.9	1.3	—	—	—	0.3	—	—	—	—
19	65.6	1.23	6.47	—	—	—	1.03	12.2	0.08	9.97	0.11	3.27	—
20	57.3	—	3.58	—	—	—	—	12.5	0.16	21.0	0.13	5.42	—
21	71.4	3.53	7.78	—	—	—	—	4.50	0.05	9.52	0.07	3.13	—
22	71.6	6.38	8.40	—	—	—	—	12.2	0.03	—	0.07	1.41	—
23	74.8	11.3	7.11	—	0.75	—	—	—	0.06	—	0.06	5.90	—
24	74.9	5.52	10.9	—	—	—	—	1.69	0.10	4.25	0.14	2.44	—
25	61.7	—	24.9	—	—	—	—	10.8	0.07	2.38	0.11	—	—
26	65.4	—	4.68	—	—	—	29.7	—	0.15	—	0.11	—	—
27	71.2	0.77	8.08	—	—	—	19.7	—	0.12	—	0.09	—	—
28	76.0	1.93	7.39	—	—	—	14.4	—	0.14	—	0.11	—	—
29	77.0	0.80	10.6	—	—	0.12	11.5	—	—	—	—	—	—
30	—	—	14.8	—	11.3	11.6	—	—	—	—	0.72	4.98	56.6
31	—	4.12	—	—	10.0	—	6.87	12.6	—	—	0.15	66.3	—

The following descriptions are added :

1. Thuringian bottle glass, medium quality, Stützerbach.
2. } Good bottle glass, origin unknown, old, has been long in
3. } contact with water.
4. }
5. Inferior bottle glass, origin unknown.
6. Soft crown, Jena, No. 359.
7. Jena normal-thermometer glass, 16<sup>III</sup>.
8. Extra light flint, Jena 788.
9. Densest flint, Jena S. 164.
10. Crown (like English), Jena 283.
11. Thuringian Glass A, from Gehlberg.
12. Bohemian potash glass.
13. Thuringian glass B, from Stützerbach.
14. Crown (like Feil's), Jena 260.
15. Thuringian glass C.
16. Thuringian glass D from Stützerbach.



17. Inferior Thuringian E.
18. Inferior Thuringian F.
19. Zinc barium crown, Jena 463.
20. Densest barium crown, Jena 634.
21. Barium crown, Jena 227.
22. Ordinary zinc crown, Jena 493.
23. Borosilicate crown, Jena 599.
24. Crown (like English), with baryta, Jena 861.
25. Potash crown, Jena 365.
26. Very dense flint, Jena 303.
27. Ordinary flint, Jena 824.
28. Light flint (like English), Jena 677.
29. Lead crystal glass.
30. Light phosphate crown, Jena, like O. 225.
31. Borate flint, Jena, like S. 8.

**The Conductivities** are always given by Kohlrausch for a standard temperature of  $18^{\circ}$ . The measurement was made after the manner of that of a mercury-in-glass standard resistance. The glass-holder employed in nearly all the experiments held 20 c.c. of liquid, and, when filled with mercury at  $0^{\circ}$ , gave a resistance of  $\cdot 0000138$  Siemens unit, a value checked by frequent repetitions. The relative conductivities of the solutions as compared with mercury at  $0^{\circ}$  were determined; and Kohlrausch uses the symbol  $k$  to denote  $10^{10}$  times this relative conductivity.

The purest water that can readily be procured in large quantities, has on this scale about the conductivity  $k = 1$ . The water usually employed by Kohlrausch was kept, after distillation, for a considerable time, in loosely covered flasks; and its conductivity ranged from  $k = 1$  to  $k = 2$ . In each case the value of  $k$  for the water was subtracted from the observed value for the solution.

**Reduction Factor  $R$ .** If a glass solution has conductivity  $k$ , and contains  $Rk$  milligrams of dissolved material per litre,  $\frac{1}{R}$  is a measure of the conducting effect per milligram of dissolved matter. Kohlrausch calls  $R$  the *reduction-factor*, and finds the following values:

Solution of	$R$
NaOH	0.22
KOH	0.28
$\text{Na}_2\text{SiO}_3$	0.50
$\text{K}_2\text{SiO}_3$	0.64

The following determinations for eleven different glasses were obtained by evaporating their solutions:

No.	18	25	5	1	16
Value of $R$	0.4	0.41	0.48	0.63	0.7

No.	7	13	11	4	12	31
Value of $R$	0.73	0.8	0.9	1.8	2.2	5.2

The large values of  $R$  for glasses 4, 12, 31 indicate that they contain matters in solution which contribute little to the conductivity; Kohlrausch suspects silicic and boric acids. There is, however, another way of accounting for a large value of  $R$  in a very dilute solution, namely this: that while, in a neutral solution, the conductivity is approximately proportional to the strength, this is not the case in acid or alkaline solutions till the strength has attained a certain amount, below which the conductivity increases more slowly than the strength.

**Water in Bottles.** Ordinary stoppered bottles of glasses 1, 2, 3, 4, 5 were charged with pure water, and moved several times a day as long as the experiments lasted. The bottles of glass 1, being new, were first rinsed quickly with water. The following table shows the course of the observations.  $M$  denotes

		5		1		2	3	4	
		$k$	$M$	$k$	$M$	$k$	$k$	$k$	$M$
After	1 day	16	0.48	—	—	—	—	—	—
„	5 days	33	1.0	1.6	0.09	—	—	—	—
„	10 „	54	1.6	2.7	0.15	—	—	—	—
„	20 „	—	—	5.0	0.27	0.8	0.6	0.20	0.04
„	40 „	—	—	—	—	1.6	0.7	—	—
„	80 „	120	3.6	12	0.65	4.0	1.7	0.49	0.09
„	160 „	—	—	22	1.2	—	—	—	—
7 hours at 80°		800	24	69	3.7	49	2.7	—	—
19	„ „	1250	37	100	5.4	93	5.2	—	—

the number of milligrams of solid matter in solution per sq. decim. of glass surface. The figures show that the increase of strength of the solution followed different courses for different glasses.

Heating to  $80^{\circ}$  quickened the process of solution very much in the cases of 5, 1, 2, but comparatively little in the case of 3. In the case of 4, which was the best glass, the value of  $k$  after ten hours at  $60^{\circ}$  had only increased by about 0.15. At  $90^{\circ}$  the increase was 2, and in the neighbourhood of  $100^{\circ}$  was about 5.

The better glasses showed improved resisting power after treatment with hot water, and also after prolonged treatment with acid.

**Etched Surfaces.** Bottles of glasses 1 and 4 were etched with fluoric acid, and then again tested for their behaviour with cold water. Their resisting power showed no material change.

**Powdered Glass.** Kohlrausch also tested all the thirty-one glasses, except 2, 3, and 6, in the form of powder. A piece of the glass was pounded in an agate mortar, and rubbed down till there was no longer a gritty feeling under the pestle, and the powder began to cake. It was estimated, from microscopic observation, that the total surface furnished by a gramme of the powder was of the order of a square metre.

In the case of each of the glasses 1, 4, 5, 7, 11, 12, the powder was put, with 100 times its weight of water, into a closed glass vessel, and frequently shaken up every day for a week. It was then allowed to settle, the liquid very carefully poured off, and a second quantity of water added equal to the first. At the end of another week, there was a second pouring off; which was succeeded in like manner by a third. The comparatively trifling action of the vessel itself on the water was known and allowed for.

The first supply of water was found, after the first few minutes, to have already dissolved an appreciable quantity of material; but the rate of solution decreased rapidly, and generally most rapidly in the most resisting glasses. The second supply began with a slower rate of solution, which, as in the case of the first, diminished with increasing rapidity; and the action of the third supply showed a similar relation to that of the second.

The powder and solution (at  $17^{\circ}$ ) were contained, with a thermometer, in a vessel with platinum electrodes; and the measurements for  $k$  were made by Wheatstone's bridge with telephone. Multiplication by  $R$  gave the amount of material dissolved. Observations were made after the lapse of 2 minutes,

1 hour, 1 day, and 1 week, from the pouring in of each supply of water.

Kohlrausch gives<sup>1</sup> a table, showing the total amount of matter dissolved off each glass, the progress of the dissolving during each week, and the ratios of the effects of the second and third waterings to that of the first. We subjoin a brief extract. The first column contains the numbers of the six glasses; the second the sum of the quantities (in mg. per litre) dissolved off the glass by the three waterings; the third column the ratio of the effect of the third watering to that of the first; the fourth column the sum of the conductivities  $k_1$ ,  $k_2$ ,  $k_3$  exhibited by the three solutions, each observed at the end of the week's action.

No.	mg./lit.	III. : I.	$k_1 + k_2 + k_3$ .
7	136	0·15	186
11	189	0·15	210
4	281	0·11	156
1	357	0·21	568
12	405	0·25	184
5	992	0·40	2070

The other glass powders were somewhat differently treated: Previous to the three wettings for a week with 100 times their mass of water, they were wetted for two days with 20 times their mass of water, and thus gave more concentrated solutions. With the worst lime silicate glasses the strength of the solution in mg. per litre was 1200, and with the best 200. With the limeless glasses, the minimum was still lower, but the maximum reached 3000, and, in the case of the borate flint, 6000. With the densest lead silicates, the quantity dissolved was vanishingly small. As, however, there was a slight increase of conductivity at first, followed by a decrease, Kohlrausch suspected that matter had first gone into solution, and then been separated; a view which was confirmed by the appearance of a firmly adhering deposit on the walls of the vessel.

As most of the solutions were not evaporated, it was not generally possible to make direct comparison of the dissolved amounts, but only of the conductivities. In the table which we

<sup>1</sup> K., II. 3567.



reproduce below,  $k_0$  denotes the conductivity of the solution obtained in the first two days, with 20-fold mass of water, and  $K$  the sum of the conductivities of the three subsequent solutions, plus  $\frac{1}{5} k_0$  (because 20 is  $\frac{1}{5}$  of 100).

Corrections have been applied, for temperature, and for the specific gravity of the glass. The small variations of temperature which occurred during the observations showed a surprisingly large influence. Kohlrausch estimates it at 10 per cent. increase of  $k$  for  $1^\circ$  of rise of temperature, and has corrected accordingly. Again, denoting by  $s$  the specific gravity of the glass, the observed value of  $K$  is multiplied by the correcting factor  $s/2.5$ , so as to reduce to a standard specific gravity 2.5. This gives values of  $K$  related to equal volumes of glass.

Glasses 1, 4, 5, 7, 11, 12 are also included in the table; the observed values of  $k_1 + k_2 + k_3$  given for them above being increased by  $\frac{1}{5} k_3$ , to make up for the absence of the two days' preliminary wetting.

To throw further light on a very important quality of glasses—the persistence of their corrosion by water, the glass powders were exposed for half a year to the attack of water, changed from four to six times during that period. They were then exposed for a week to the action of 100 times their mass of fresh water. The conductivity of the solution obtained by this last wetting is denoted by  $k_\infty$ , and given in the fourth column of the table.

In those cases in which the reduction factor  $R$  was known, the total quantity of matter that went into solution during the half-year was calculated; and it is given in the last column, as a percentage of the mass of glass powder from which it was derived.

The table is divided by horizontal lines into three compartments, of which the second contains the lead glasses, and the third the non-silicious glasses. The order of arrangement in each compartment is according to the values of  $K$ .

The table confirms the result, previously deduced from hot-water experiments, that solubility is mainly determined by the gross content of alkali. Potash, however, appeared more conducive to solubility than soda.

The order of the lead glasses 9 to 29 follows a very simple law; the solubility increases with the content of alkali, with the

exception of 29, which stands out prominently by the largeness of its  $K$ ; perhaps owing to its large content of potash.

Boric acid in combination with silicic acid seems to check solubility. The borosilicate 23 is a well-marked instance. It is composed almost entirely of silicic acid, boric acid, and alkali, and has but slight solubility. The borate flint No. 31, on the other hand, shows an amazing amount of solubility. The phosphate No. 30 shows much the same behaviour as the silicate glasses.

No.	$k_0$	$K$	$k_\infty$	Per cent. Dissolved.
19	120	50	8	—
20	180	80	10	—
21	210	130	15	—
22	270	130	7	—
4	—	170	—	—
7	270	180	10	2.0
10	380	200	80	—
23	490	220	8	—
11	360	220	7	2.7
12	320	230	7	7
13	440	230	40	3.5
14	420	320	12	—
15	730	420	50	—
16	600	460	20	5
24	680	570	30	—
1	—	640	—	—
17	1200	860	60	—
18	2600	2200	200	13
5	—	2300	—	—
25	7000	6800	500	30
9	5	1	0	—
26	40	9	0	—
27	300	100	7	—
28	360	130	7	—
8	350	190	6	—
29	800	350	30	—
30	500	320	20	—
31	1000	1000	60	50

The solutions, with the exception of those derived from the phosphate glass, showed more or less alkaline reaction.

The behaviour of the crown glass No. 10 (called English crown, but made at Jena) is peculiar for the largeness of its  $k_{\infty}$  compared with its  $k_0$  and  $K$ . At first it ranks among the best glasses; but six months' washing improves it so little that at the end it is low on the list.

**Influence of Temperature.** In the case of some of the powdered glasses, after they had been a long time in water, variations were made in the temperature; and it was found that the rates of dissolving at

	10°·8	17°·2	23°·6
were as	1	2·7	7·4

This large influence of temperature is in conformity with earlier observations by E. Pfeifer.

Kohlraush, after keeping a number of powdered glasses in cold water—(occasionally renewed)—for half a year, warmed them up, in their last solutions, to 80°, and maintained them at this temperature for seven hours. He then compared the conductivity of the last solution with the sum of the conductivities of all the solutions obtained from the same glass during the preceding half-year. It amounted, on the average, to nearly half this sum; the ratio varying greatly for different glasses.

**Hygroscopic Behaviour of Powdered Glass.** Eleven specimens of glass in the form of very fine freshly ground powders were placed, in quantities of about 1 gm., on a small platinum dish, for two days, beside water, under a bell glass, and were then again weighed, to show the amounts of moisture they had acquired

No.	Gain per cent.	$K$ .	$RK$ .
12	2	230	506
11	2	220	198
7	2	180	131
13	4	230	184
15	5	420	—
16	5	460	322
1	5	640	403
17	7	860	—
18	9	2200	880
5	10	2300	1104
25	18	6800	2788

from the air. These gains of weight, expressed as percentages of the original weights, are given in the second column of the foregoing table. By way of comparison with these, the third column contains the values of  $K$  already given for the same glasses; and the fourth column, in the case of those glasses for which the "reduction factor"  $R$  is known, contains the product  $RK$ , which represents quantity of matter dissolved. It will be seen that, with the exception of the Bohemian potash glass 12 (which has 82 per cent. of silica), the order of arrangement is substantially the same for the fourth column as for the second. A fair estimate of the solubility of a glass in water can therefore be made, from its gain of weight, when exposed in the form of powder to moist air under the above conditions.

#### Improvement of Surface by Long Contact with Water.

One of the difficulties in the way of getting pure water is the influence of the air in distillation. Kohlrausch has shown that the electric conductivity of water can be very largely diminished by distilling in vacuo. The apparatus which he employed (Fig. 28)

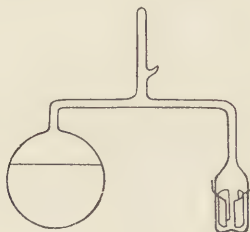


FIG. 28.

is of the nature of a water hammer. A glass globe 100 to 200 cm. in diameter serves as the retort, and is connected by a T-shaped tube with a small vessel which serves as the receiver. This contains a pair of platinum electrodes for measuring the resistance of the distillate. By the use of a warm bath at  $30^{\circ}$  to  $45^{\circ}$ , and a cold bath at  $0^{\circ}$  to  $-8^{\circ}$ , the requisite 6 to 8 c.c. of water can be distilled over, and its resistance measured.

By distillation with this apparatus,<sup>1</sup> under a pressure of about .01 mm. of mercury, Kohlrausch succeeded in obtaining water of so low a conductivity as  $k = .25$ .<sup>2</sup>

<sup>1</sup> *Ann. d. Phys. u. Chem.*, 44. 48 (1885).

<sup>2</sup> This is relative to mercury at  $0^{\circ}$  taken as having  $k = 10^{10}$  (see p. 351).



The vessel used in the experiment was then washed out with water for 10 years. At the end of that time, the surface of the glass had so much improved that Kohlrausch and Heydwiller (1894) were able to obtain water of much greater purity than before.<sup>1</sup>

The vessel was charged, on 5th January 1894, with water of conductivity  $k = 0.75$ , and exhausted for  $1\frac{1}{2}$  hours. The remaining air bubble was of the size of a pin's head; whence the pressure over the water was estimated at  $\frac{1}{4000}$  mm. The value of  $k$  had now fallen to about a quarter of its original amount. During the next two months, 45 distillations were performed, which gave continually improving water. The store of water in the globe, at the same time, as was to be expected, increased in conductivity, but only very slowly, showing that the long-continued washing had rendered the surface of the glass very insoluble.

An outline of the course of these experiments, which are very promising as regards the obtaining of unusually pure water, is given in the following table. The first column indicates the order of succession of the distillations whose results are given.

No.	Day.	$k$ in	
		Retort.	Receiver.
1	0	0.17	0.075
3	1	0.18	.069
7	10	0.35	.058
13, 14, 15	16	0.43	.044
20, 21	22	0.53	.0425
23	23	0.55	.0412
27	24	0.57	.0409
31	31	0.69	.0409
35	39	0.82	.0405
36	39	0.82	.0404
42	55	1.05	.0407

Thus, after about 30 distillations, the conductivity had practically attained its limit,  $k = .04$ ; whereas distillation in air never gives less than  $k = .7$ .

The kind of glass with which this success was attained is not stated.

<sup>1</sup>K. u. H.

**143. Action of Dissolved Alkali on Glass.** The mode of attack of glass by alkaline solutions under various conditions has been discussed in general terms by Foerster, mainly on the basis of his own observations.<sup>1</sup> The following are his inferences.

As the action of water on glass sets alkali free, no sharp line can be drawn between the action of water and that of dilute solutions of alkali. The alkali extracted by the water from the glass, as long as it remains close to the glass and only moderately diluted, strengthens the attack in two ways: first by producing swelling up of the surface; and secondly (especially at high temperatures) by dissolving silica. When the alkali has spread by diffusion to a distance from the glass surface, it is usually so much diluted that it is no longer in a position to strengthen the attack.

Very dilute solutions of alkali—say millinormal—attack glass no more actively than pure water. If however the dilution is not so excessive, it strengthens the attack, and this effect increases somewhat rapidly with increasing concentration.

In lime-alkali glasses, decomposition is effected by taking out alkali-silicate, while lime-silicate is left. Pure 1 per cent. soda lye at 100° dissolves so much from ordinary lime glass that the surface is dulled by the lime silicate which remains. Further concentration of the alkaline solution causes the lime silicate to be also attacked. Soda lye of double normal strength dissolves lime-alkali glass as a whole.

From this point onwards, further concentration produces, in no case, any material strengthening of the attack. The solubility of glass in lye of either soda or potash, shows a decided falling off at ordinary temperatures when the concentration is made very high, and at 100° remains nearly constant. Highly concentrated solution of ammonia, whether at ordinary temperatures or at 100°, attacks glass much less than a weaker solution. Hence, for good keeping of caustic alkalis in glass vessels, the solutions should be as strong as possible.

As regards strength of attack on glass, the chief alkaline solutions take the order (from stronger to weaker) soda lye, potash lye, ammonia water, baryta water.

Glasses do not as a rule differ nearly so much in susceptibility to attack by alkaline solutions as by water. The differences are usually in the same direction, for glasses of any one type.

<sup>1</sup> F., IV. 459.

The above general statements are largely based upon an investigation carried out by Foerster with four lime glasses.<sup>1</sup> These glasses, which were representative of the kinds then chiefly used commercially, showed considerable uniformity of composition. Better materials for the comparison of different types of glass were furnished by his later research.<sup>2</sup> It deals with 12 out of the 14 glasses enumerated in Art. 139, and the numbers by which they are there designated are here retained.

As the actions of different alkalis upon glass are qualitatively alike, it was thought sufficient to make the tests with soda, which is the most active of them. Flasks of the 12 glasses were charged with soda lye of double normal strength, free from silica, and were kept at 100° for three hours in a paraffin bath. Their loss of weight under this treatment was observed, and is given in the second column of the subjoined table, in mg. per sq. decim. In the third column are reproduced, for comparison, the quantities of alkali dissolved out of the same glasses in three hours by water at 80°, expressed in thousandths of a mg. of soda per sq. decim.<sup>3</sup>

No.	Soda lye at 100°.	Water at 80°.
1	67.3	2.7
2	39.7	6.3
3	35.4	28.4
4	37.5	28.2
6	39.8	56
7	37.7	45
8	38.5	50
9	42.4	66
10	46.5	65
11	31.3	98
16	46	654
17	58	350

We find here some marked exceptions to the similarity of behaviour towards water and towards alkaline solutions. Though, in the majority of instances, the two sets of values increase

<sup>1</sup> F., I. 2497.

<sup>2</sup> F., V. 384.

<sup>3</sup> For glass 5, which resembles that employed by Stas, and is not included in the table, the two values are 37 and 27, according to information given in F., II. 2922.

together, the borosilicate 1 = 59<sup>III</sup>, which is the most resisting of all against water, is the least resisting of all against soda lye. Foerster attributes this to its large content of boric acid, and remarks that, even with decinormal soda lye, it lost 45 mg., as against 26 mg. lost by lime glass. The two zinc-containing glasses 2 = 165<sup>III</sup> and 10 = 16<sup>III</sup>, especially the former, behave worse with soda lye than would be expected from their good behaviour to water. On the other hand, the soda glass 11, which contains alumina and a large amount of lime, is the best of all for resisting soda lye, though weak in resistance to water.

It is only in dealing with glasses of one and the same type, that their relative resistances to alkaline solutions can be inferred, even roughly, from their resistances to water.

**144. Action of Acids on Glass.** Earlier experiments on the action of acids upon glass having led to contradictory conclusions, Foerster took up the subject anew, and succeeded in arriving at definite results. Besides the detailed account of his observations,<sup>1</sup> he has published comprehensive summaries.<sup>2</sup>

**Experiments at 100°** were made with round flasks of three lime glasses *A*, *B*, *C*, identical with Nos. 8, 15, 16 of Art. 139. No. 17, under the name of *H*, was included in some later experiments. After cleaning, drying, and weighing, the flasks were heated in a paraffin bath at 100°, and filled with acid at 100°. After six hours at this temperature, the acids were removed, the glasses cleaned and dried, and their losses of weight determined.

The acids thus employed were;—sulphuric acid, in 6 different degrees of dilution, and pure; nitric acid in 5, hydrochloric in 5, and acetic in 3 different degrees of concentration. Similar experiments were also made with pure water, for comparison.

It was found that, for one and the same glass, the loss of weight was the same, whether the dilute acid was sulphuric, nitric, hydrochloric, or acetic, and was the same whether the solution was normal or millinormal or tenfold normal. A considerably higher degree of concentration gave weaker action. In all cases the actions were much weaker than that of pure water. With glass *A* the action never exceeded  $\frac{1}{15}$ , and with glass *C* about  $\frac{1}{3}$  of the action of pure water.

<sup>1</sup> F., III.<sup>2</sup> F., II. and F., IV.



Foerster concludes that the acid in the solution exerts no sensible amount of direct action on the glass, but merely modifies the action of the water on the glass.

**Experiments with Superheated Acids** were made, in the following manner, on three lime glasses, *D*, *E*, *F*, of which *E* and *F* were described as good, and *D* as inferior. Cylindrical bits of tube, of the three glasses, were dried at  $100^{\circ}$ , and weighed, then enclosed with the acid solutions in larger tubes, heated for four hours in a glycerine bath, either at  $160^{\circ}$  or  $190^{\circ}$ , and afterwards tested for loss of weight.

Here also it was found that the strength of attack was the same with such different acids as sulphuric and acetic, provided that the concentration, reckoned by the number of gram equivalents in a litre of water, was the same. The influence of concentration became more conspicuous at these high temperatures, and was still in the direction of diminished attack for increased concentration.

A similar result was obtained, when coarsely pounded lime glass was exposed, for six hours, to the action of hydrochloric acid of different strengths, at temperatures between  $260^{\circ}$  and  $270^{\circ}$ . Glasses *D*, *E*, *F*, treated in this way, were again much more strongly attacked by pure water than by the acids.

**Explanation of the Behaviour of Lime Glass to Acid Solutions.** To explain these results, Foerster starts from the assumption that the acids exert no direct action on the glasses, and that the attack is exclusively due to the water which is present. This view leads naturally to the conclusion that a larger content of acid weakens the attack, by diminishing the concentration of the attacking water.

A further and more important reason for the influence of acids, is furnished by the following consideration: The first action on glass consists in taking out alkali. This alkali then aids further attack, as explained in previous articles. The presence of an acid neutralises this alkali, and prevents it from aiding attack; and the neutralisation is effected more quickly and more completely in concentrated than in weak solutions. The influence of concentration is greatest when alkali is being most quickly set free, and it is set free most quickly at high temperatures.

The action of water on glass, though influenced by the presence of an acid, is not thereby altered in character. The whole difference

turns upon the fact that the accumulation of free alkali in the solution is checked. But the alkali which is set free in large quantity by hot water, dissolves a large quantity of silica and brings it into solution. This action is likewise checked, when acid is present to neutralise the alkali. It is accordingly found that alkali is far more completely washed out of glass by acid solutions than by pure water.

It must not be supposed that the above conclusions are *universally* applicable to silicates. There are a few silicates of lime and potash which are directly attacked by acids, especially by hydrochloric acid. It attacks them far more powerfully than water; and the strength of attack increases with the concentration. Foerster was able to establish the existence of this exceptional behaviour in the case of Wollastonite ( $\text{CaSiO}_3$ ) and a Labradorite. The fused metasilicate  $\text{Na}_2\text{SiO}_3$  was also more strongly decomposed by concentrated than by dilute acids, and more strongly by these than by water. On the other hand, a melting, of the composition  $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ , conformed to the rules for glasses. From a review of all the facts, Foerster concludes that the ordinary behaviour of glass towards acid solutions is due to its large content of silica. In fact, glasses with exceptionally small content of silica are strongly attacked by dilute acids.

**Behaviour of Lead Glasses.** With three lead glasses *G*, *H*, *I*, Foerster made experiments at  $100^\circ$  similar to those made with the lime glasses *A*, *B*, *C*. The flasks of the glass *I*, which contained 33.8 per cent. of lead, were made at Jena. It was found, just as in the case of the lime glasses, that dilute sulphuric, hydrochloric, and acetic acids had less action than pure water, and that the nature and concentration of the acid made practically no difference. Foerster recalls the fact that the resisting power of lead crystal glass to acids is increased by long-continued exposure to acids. Were it otherwise, the use of this material for wine glasses would long ago have been given up. Against pure water these glasses are more resisting than lime glasses.

On the other hand, flint glasses poor in silica and rich in lead exhibit entirely different behaviour. The Jena flint glass, of composition

$\text{SiO}_2$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{PbO}$	$\text{MnO}$	$\text{As}_2\text{O}_5$
39.85	0.5	6.5	52.8	0.05	0.3

reduced to coarse powder, was introduced, in quantities of 10 gm., into 100 c.c. of water, normal solution of acetic acid, and normal solution of hydrochloric acid; and gently boiled for six hours, with backflow cooling. The water acted only very slightly, but the acids very strongly, and the hydrochloric beyond all comparison more strongly than the acetic. The powder in the hydrochloric lost 12 per cent. of its weight, and the silica left behind gave the surface a porcelain-like appearance.

**Behaviour of Glasses 16<sup>III</sup> and 59<sup>III</sup>.** These two glasses, which (Art. 139) differ materially in composition from those of which we have been speaking, were tested by Foerster for their behaviour with normal, five-fold normal, and ten-fold normal acids ( $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{C}_2\text{H}_4\text{O}_2$ ) at  $190^\circ$ , it having been found that they were very little attacked by acid solutions at  $100^\circ$ . They were also tested with pure water for comparison.

With water they lost less weight than the good lime glasses *E*, *F*; and with acids less than with water. In the case of 59<sup>III</sup> the attack by acids diminished as the concentration increased; the glass thus resembling the lime glasses in its behaviour. With sulphuric and acetic acids 16<sup>III</sup> also behaved in this way; but hydrochloric acid attacked it more powerfully with increasing concentration, as shown by the comparative figures:

Normal.	Five-fold normal.	Ten-fold normal.
16	21	24

Foerster infers that this glass was directly attacked by hydrochloric acid, and finds a confirmation in the circumstance that the bits of tube after the experiment showed dull surfaces.

**Action of Pure Sulphuric Acid on Glass.** With the lime glasses *B* and *C*, Foerster made the following experiment: Bits of tube were suspended by platinum wire in sulphuric acid, which was gently boiled for six hours in flasks of very good glass. The resulting loss of weight in mg. per sq. decim. was 1.5 for *B* and 2.6 for *C*. These figures show that boiling sulphuric acid is much weaker in its attack than boiling water.

The vapour of sulphuric acid also acts on glass, and more strongly as the temperature rises. Foerster remarks, in connection with this fact, that the sulphuric acid contained in the products of combustion of coal, and of illuminating gas, attacks



glass, giving it a white coating of alkali sulphates, easily removable by water.

**145. Action of Saline Solutions on Glass.** The four lime glasses mentioned in Art. 143 were also tested for their behaviour to various solutions of salts.<sup>1</sup> Trials with solutions of carbonates of alkalis showed that they may, in some cases, attack a glass more strongly than solutions containing equivalent quantities of the caustic alkalis. Carbonate of soda usually acts much more powerfully than carbonate of potash. Special attention is called by Foerster to the fact that, according to the observations made with these four glasses, a content of even 3 per cent. of alumina largely increases resistance to carbonates of alkalis, in the case of a glass containing much alkali and little lime. This effect he ascribes to the circumstance that alumina is insoluble in carbonates of alkalis. He mentions that, in experiments on the action of very dilute alkaline solutions on glass, irregularities are apt to be introduced by the taking up of carbonic acid from the air during the necessary operations.

Experiments with other salt solutions soon showed that, in general, the greater or less resistance of a glass to attack by carbonates of alkalis, is no criterion of its behaviour towards salts of other kinds.

A solution of sulphate of soda had but little effect on any of the four glasses.

They were much more strongly attacked by phosphate of soda; and here again the glasses that contained alumina were distinguished by their greater resistance.

• Exact knowledge of the action of very concentrated salt solutions on glass is not of much practical importance. The solutions employed in analytical work are often so dilute that their action on glass does not sensibly differ from that of water. The relations become more complicated when we have to do with solutions which are not neutral, but acid or alkaline.

Whether there is any glass pre-eminent for high resisting power against the greater number of important chemical reagents, must at present be left an open question.

**Attack by Carbonate of Soda.** Foerster subsequently<sup>2</sup> experimented on a greater variety of glasses, for their behaviour

<sup>1</sup> F., I. 2510.

<sup>2</sup> F., V. 384.



to a solution of carbonate of soda. The glasses employed were 11 out of the 14 described in Art. 139, namely Nos. 1, 2, 4, 6, 7, 8, 9, 10, 11, 16, 17. They are all included among those tested by soda lye at 100° and by water at 80° (Art. 143).

Globular flasks of these 11 glasses were charged with carbonate of soda solution of double normal strength, heated for three hours in a paraffin bath at 100°, and then tested for loss of weight. The subjoined table gives, in the second column, these losses reduced to mg. per sq. decim. of glass surface. The third and fourth columns are reproduced from Art. 143 for comparison. The time of exposure was three hours in all three cases, and the circumstances were similar; but whereas cols. 2 and 3 give total loss, col. 4 gives only loss of alkali, reduced to equivalents of soda. The soda lye, like the carbonate of soda solution, was of double normal strength.<sup>1</sup>

No.	Carb. of soda solution at 100°.	Soda lye at 100°.	Water at 80°.
1	23·5	67·3	2·7
2	17·6	39·7	6·3
4	59·5	37·5	28·2
6	76·9	39·8	56
7	79·2	37·7	45
8	73·0	38·5	50
9	79·4	42·4	66
10	23·0	46·5	65
11	40·7	31·3	98
16	45	46	654
17	51	58	350

Glasses 4, 6, 7, 8, 9, which consist mainly of silica, alkali, and lime, are very strongly attacked by the carbonate of soda solution; much more strongly than by the soda lye. The best resisting glasses against the carbonate of soda are numbers 1, 2, 10. The fact that they contain alumina is not alone sufficient to account for this; for 11 and 16 also contain alumina, and yet show only moderate resistance.

**146. Jena Laboratory-Glass** (Gerätéglass). This is a boric acid glass with remarkable power of withstanding changes of

<sup>1</sup> For No. 5 glass, which was similar to that used by Stas, Foerster elsewhere (F., II. 2922) gives 59, 37, 27 as the corresponding three values.

temperature (see Art. 108). Foerster makes a passing allusion to it, with the remark that it is even less attacked by water than the glass used by Stas.<sup>1</sup> Fuller information has been published by F. Kohlrausch,<sup>2</sup> who tested this glass along with two varieties of a Jena melting containing no alkali; the compositions of these latter, in equivalents per cent., being

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	ZnO	BaO	B <sub>2</sub> O <sub>3</sub>
I.	65	3·3	4·6	12	15
II.	68	3·7	3·7	12	13

The specimens to be tested were rubbed down to quite fine powders, and then shaken up with a hundred times their weights of water. The solutions thus gradually formed were tested for electric conductivity in the manner described in Art. 142. The results for these three glasses are given in the following table, in the columns headed I., II., G. (G standing for Geräte glass, which in the English catalogues is called "Laboratory glass"). The table also includes results obtained in the same way for five other glasses mentioned in Art. 142. The values given denote, as in Art. 142, the electric conductivity  $k$ , so defined as to have the value  $10^{10}$  for mercury at 0°. The values in the line at the foot of the table apply to the solutions obtained, by pouring away the first solutions after the lapse of the six days mentioned, giving second supplies of pure water equal to the first, and observing after the lapse of another week.

First supply after	I.	II.	G	4	5	7	11	12
2 minutes, - - -	9	6	22	35	120	46	55	33
1 hour, - - -	14	11	26	44	260	62	71	41
1 day, - - -	18	16	33	77	580	88	104	75
6 days, - - -	22	18	38	99	850	111	130	97
Second supply after } 1 week,	—	7	—	30	570	34	36	42

Judged by these values, glasses I., II., and G. have much greater resisting power against cold water than any of the rest. But the conductivities do not truly represent the quantities of dissolved

<sup>1</sup> F., V. 396.

<sup>2</sup> K., III. 3000.

matter, and are too favourable to the first three glasses; as boric acid, which they largely contain, has relatively small conductivity in solution. But even after correction is made on this account, they still retain a distinct superiority over the other glasses.<sup>1</sup>

**The Good Preservation of Water in Jena Gerätéglass** was shown by Kohlrausch in the following way.<sup>2</sup> Two new bottles of this glass were left in running water for about a quarter of an hour; and then filled with very pure water of conductivity  $k=2$ , and left, slightly covered, at the temperature of the room. The amounts of increase in  $k$  were

Days elapsed	2	7	23	62	200
In 1st bottle	·06	·17	·20	·23	·35
In 2nd bottle	·02	·04	·06	·14	·30

These figures give, for the matter taken up from each square decim. of surface, only half the amounts which Kohlrausch had previously found for the best bottle-glass that he had ever tested, although that glass had the advantage of having been seasoned by long use.

Kohlrausch also made experiments on the behaviour of this glass to **hot water**.<sup>3</sup> The above-mentioned solution, with the powdered Gerätéglass in it, was kept for three days at 60°. It then, on being cooled to 18°, showed the value  $k=46$ . Being then kept for four hours at 93°, it showed  $k=108$ . The solution was then, after decantation, evaporated, and found to have contained 194 mg. per litre. This gives 1·8 as the value of the "reduction factor"  $R$  (Art. 142). The residuum was only very slightly hygroscopic.

A small bottle of the glass, filled with water, and maintained for 16 hours at between 50° and 60°, showed a loss of 0·2 mg. per sq. decim. of surface; which was increased to 0·8 by two hours' further heating at 100°. Kohlrausch winds up by saying, "These results are likewise considerably better than for any other glasses known to me."

**Use in Quantitative Analysis.** Reinitzer (see reference to

<sup>1</sup> Kohlrausch several times remarks that the alkali-free kinds of glass powder, after long exposure to water, formed a very firm crust on the bottom of the vessel. It is interesting to compare this behaviour with that of water-glass, as described at page 328.

<sup>2</sup> K., III. 3002.

<sup>3</sup> K., III. 3002.

authorities in Art. 130) published in 1894 a memoir entitled "Contributions to Quantitative Analysis," containing results of many years' experience in large chemical works. The last section of the memoir treats of the attack of water and aqueous solutions upon glass vessels during boiling.

About 300 c.c. of distilled water were mixed with a little lime water in a boiling flask of ordinary soft glass, and, after boiling off the carbonic acid, titrated violet with decinormal hydrochloric acid. The liquid was then boiled for about 15 minutes, and turned pure blue. When neutrality was restored, the acid consumed was found to have increased from 12.74 to 12.77 c.c. Two repetitions of the boiling brought the amount up to 12.80 and 12.90 c.c. The influence of the alkali dissolved from the glass was thus very perceptible.

700 c.c. of distilled water, in a new flask of Bohemian glass by Kavalier, were boiled for four hours, the water evaporated being condensed back. To neutralise the alkali dissolved from the glass, 9.53 c.c. of decinormal acid were required. A further quarter of an hour of boiling raised the consumption to 10.22 c.c.; and another quarter of an hour raised it to 10.92 c.c. "The impurity introduced into large quantities of liquid by 15 minutes' boiling, is thus so considerable that it could be distinctly measured with normal solution, and the employment of decinormal is quite unnecessary."

The experiment was then repeated with a retort of the best very infusible potash glass of the same maker. After four hours' boiling, 1.09 c.c. of decinormal acid had to be added to neutralise the alkali. As the boiling went on, the quantity had to be increased in 10 minutes to 1.14 c.c., and in a further 7 minutes to 1.16 c.c. In this glass, then, with 10 minutes' boiling, small quantities of alkali can be measured by decinormal acid, without material error.

Reinitzer goes on to say, "It was a matter of great interest to me, after these results, to test, in a similar way, the new Jena laboratory-glass, as regards its suitability for the more delicate work of quantitative analysis, especially for the measurement of small quantities of alkali in large quantities of liquid. In a new flask of this glass, 700 c.c. of distilled water were boiled as before for four hours, and then tested, with decinormal acid and litmus, for the quantity of dissolved alkali.



"0.13 c.c. of acid was consumed. After 18 minutes further boiling, the whole consumption had reached 0.18 c.c. of decinormal acid.

"These figures show clearly that the new Jena laboratory-glass is far superior, in resisting power against boiling water or dilute saline solutions, even to the *best* Bohemian potash glass (which is never used for boiling flasks and beakers). It is about eight times as good as the very infusible Bohemian potash glass, and about eighty times as good as the ordinary Bohemian laboratory-glass. It is accordingly beyond doubt that, by this new glass, the resources of the chemist have been enriched to an extraordinary extent. Hitherto the titration of large quantities of weakly alkaline liquid (for example, the measurement of the alkalinity of natural water) has been rendered quite erroneous by the change produced in the water by boiling in glass vessels; but it can now be performed with the greatest sharpness. Since, as I have previously shown, the most careful boiling away of the carbonic acid is always necessary in order to obtain, with decinormal solutions, definite and sharp changes of colour in large quantities of liquid, it is quite clear, having regard to the demonstrated influence of boiling in glass vessels, *that the test by decinormal acids for alkali has now for the first time, by the use of vessels of Jena laboratory-glass, really attained the accuracy which has hitherto been claimed for it.*"<sup>1</sup>

<sup>1</sup> The passage italicised is leaded in the original memoir. It is followed by a practical illustration, which Dr. Hovestadt reproduces, but which is couched in too technical language to be of general interest to our readers.

Art. 147, "On Surface Tension of Water in Capillary Tubes of Different Glasses," describes experiments by Volkmann (see references in Art. 130) to determine whether capillary elevation of water in glass tubes is influenced by the nature of the glass. The conclusion is in the negative, and the discussion lacks interest.

## CHAPTER XI.

### ELECTRIC AND MAGNETO-OPTIC PROPERTIES OF GLASS.

**148. Insulating Power of Different Glasses.** Differences in the insulating properties of different glasses depend mainly on their chemical behaviour towards water. Glasses easily attacked by water are bad insulators.

F. Kohlrausch has investigated this point by comparative observations, and sums up his results in the following brief communication to the German Chemical Society.<sup>1</sup>

"That chemically bad glasses insulate badly is a fact which has been long known. That this is due to the Faraday water-film, acting in concert with the alkali, has been thoroughly established by Warburg and Ihmori.<sup>2</sup> I will merely add some information as to how glasses group themselves from this point of view. I suppose the glasses in question to have been for some time in water, then rinsed with distilled water, and dried in the sun, or in an oven, or in some such way.

"At the outset all will insulate well; but after some time considerable differences will show themselves.

"Decidedly bad glasses will then be recognizable by their discharging a gold-leaf electroscope almost instantly when the percentage of saturation in the air is between 50 and 60, and in a short time (1 sec. or 2 sec.) when it is between 40 and 50. With glasses of medium quality, as well as with lead crystal and

<sup>1</sup> *Ber. d. deutsch. chem. Ges.*, 26. 3002 (1893).

<sup>2</sup> *Ann. d. Phys. u. Chem.* 27. 481 (1886).

Jena thermometer glass, the corresponding percentages of saturation will be about 20 higher.

"The Thuringian glass made at Gehlberg<sup>1</sup> insulates perfectly up to 40 per cent. of saturation, fairly well at 60 per cent., and discharges in a few seconds at 80 per cent.

"With Bohemian potash-glass,<sup>2</sup> which, at least as regards quantity of alkali dissolved, must be reckoned among good glasses, no traces of conduction appeared till the percentage was above 50 per cent.; and the insulation was still fairly good at 75 per cent.

"At the head of all stood the alkali-free Jena glass,<sup>3</sup> which insulated perfectly at above 60 per cent., and well even at 80 per cent. of saturation.

"It would be convenient if this glass were obtainable commercially for some purposes."

**149. Transparency for Röntgen Rays.** Röntgen himself announced that glasses of different composition behave differently as regards the transmission of the X rays—in particular, that lead glasses show larger absorption than glasses free from lead.

Winkelmann and Straubel<sup>4</sup> carried out an extended investigation of various properties of the Röntgen rays, which included the testing of a large number of glasses for facility of transmission. The rays, before falling on the sensitive photographic film, had to pass through one or more of the plates to be tested. These were of 23 different glasses, and their total thickness was 2·9 mm.; their common area being about 2 sq. cm. Most of them are included in the list of Winkelmann's glasses, which we have given, with their compositions, in Art. 67; and the identities are indicated in the following list, which is arranged in order of transparency, 1 being the most and 23 the least transparent.

1 = 5W.	7 = 52W.	13	19 = 21W.
2 = 49	8 = 6	14	20 = 47
3	9 = 84	15 = 32W.	21 = 23
4	10 = 90	16 = 8	22 = 33
5 = 27	11 = 25	17 = 13	23 = 69
6 = 27	12 = 28	18	

<sup>1</sup> Like No. 11, Art. 142.

<sup>2</sup> No. 12 of Art. 142.

<sup>3</sup> Represented by specimens I. and II., Art. 146.

<sup>4</sup> *Ann. d. Phys. u. Chem.*, 59. 324 (1896).

No. 3 is described as a uranium glass of unknown composition. No. 4 is a plate glass having approximately the composition

$\text{SiO}_2$	$\text{Na}_2\text{O}$	$\text{CaO}$	$\text{Fe}_2\text{O}_3 + \text{AlO}_2$	
75	15	8	2	per cent.

No. 13 had the same composition as 12 = 28W, except that the percentages of  $\text{SiO}_2$  and  $\text{As}_2\text{O}_5$  were greater by 0.1, and the percentage of  $\text{BaO}$  less by 0.2.

No. 14 was an antimony glass, of composition

$\text{SiO}_2$	$\text{B}_2\text{O}_3$	$\text{K}_2\text{O}$	$\text{Sb}_2\text{O}_3$
53.5	20	6.5	20

No. 18 agreed with 85W, except that, instead of 10.1  $\text{ZnO}$ , it had 10.1  $\text{PbO}$ .

The investigation thoroughly confirmed Röntgen's conclusion that the presence of lead oxide increases absorption. It further showed that baryta has a similar effect. No. 21 contains no lead, but 42 per cent. of baryta. The antimony oxide in No. 14, and the zinc oxide in No. 15, seem also to diminish transparency.

**Influence of the Several Components.** To obtain further light on the action of the most important glass-forming oxides, Winkelmann and Straubel experimented directly on the transparency of these oxides or their salts. The substances were reduced to powder, and equally thick layers of powder were compared.

*A.* The most transparent were: boric acid, nitrate of soda, carbonate of soda (of 97 per cent.), alumina.

*B.* Of intermediate transparency: nitrate of potash, zinc oxide, sand, carbonate of potash.

*C.* The least transparent were: lead oxide, minium, antimony oxide, barium nitrate.

The difference between *B* and *C* was greater than that between *A* and *B*. These results confirmed and extended those deduced from comparison of the glasses.

**Rare Earths.** Finally, experiments on the influence of the oxides known as rare earths became possible; Schott having introduced these materials, in quantities of from 5 to 10 per cent., into a number of new meltings, otherwise agreeing in composition with glasses previously made. For example, the



composition of a zircon glass is given by Winkelmann and Straubel as

SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>5</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	ZrO <sub>2</sub>
60	8	0.2	5.3	14.5	2	10

The first point tested was, whether these glasses possessed, like fluorite, the property of transmuting the X rays.<sup>1</sup> The conclusion was distinctly in the affirmative as regards zircon. A weaker action of the same kind was shown by a glass containing didymium, and by one containing erbium. No such effect was shown by glasses containing beryllium, uranium, cerium, or thorium.

Transparency for the X rays was then tested; and trustworthy conclusions were obtained from those pairs of glasses whose compositions were identical except in content of the rare earths; the rare earths in question being cerium, didymium, zircon, thorium. To intercept the fluorescent rays, a thin sheet of paper was interposed between the glass under examination and the sensitive film. The order of transparency (from greatest to least) thus found for the glasses was:

Cerium, didymium, zircon, thorium.

Without the interposed paper the order was:

Zircon, didymium, cerium, thorium.

**150. Special Glass for X Ray Transmission.** Soon after the publication of Röntgen's discovery, Schott<sup>2</sup> devoted his attention to the preparation of a glass which should be specially transparent to the new rays. As a preliminary step, he determined the order of arrangement of the undermentioned oxides and carbonates to be

Li <sub>2</sub> CO <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	CaO
		Mn <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>5</sub>	BaCO <sub>3</sub>	PbO		

a result which confirms the previously accepted rule that transparency follows the inverse order of the atomic weights. Experiments on this basis led Schott to a glass of composition

SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>5</sub>	Na <sub>2</sub> O
39.6	30	20	0.4	10

<sup>1</sup> See *Ann. d. Phys. u. Chem.*, 59, 336-343.

<sup>2</sup> *Beiblatt zur Zeitschr. f. Instrum.*, Heft 13, 1899.

Photographic tests showed this glass to be distinctly more transparent to the X rays than the Gehlberg glass used by Gundelach.

Gundelach took in hand the preparation of X ray tubes of the new glass; but scarcely any difference could be detected between their effects and those given by ordinary tubes. The glass has therefore not been put upon the market. The effectiveness of X ray tubes is, in fact, much more dependent on other properties than on transparency.<sup>1</sup>

**151. Dielectric Constants of Different Glasses.** The "dielectric constant," or "permittivity," or "specific inductive capacity" of glass has been a frequent subject of investigation. The following are some of the principal determinations for various kinds:<sup>2</sup>

3.0 to 3.24	-	Gordon,	-	-	-	<i>Phil. Trans.</i> , 1879, 1. 417.
6.6 to 9.1	-	Hopkinson,	-	-	-	" " 1878, 1. 17; 1881, 2. 385.
3.3 to 6.34	-	Schiller,	-	-	-	<i>Pogg. Ann.</i> , 152. 555 (1874).
6.46 to 7.57	-	Winkelmann,	-	-	-	<i>Wied. Ann.</i> , 38. 161 (1889).
6.88 to 7.76	-	Donle,	-	-	-	" " 40. 307 (1890).
3.6 to 25.3	-	Quincke,	-	-	-	" " 19. 556 (1883).
6.1		Wüllner,	-	-	-	<i>Exper. Phys.</i> , 4 Aufl., 4. 333 (1886).
7.5		Romich & Nowak,	-	-	-	<i>Weiner Ber.</i> (2), 70. 380 (1874).

The specifications of the glasses tested have not in general been very definite.

Winkelmann, with the view of determining the influence of chemical composition, made comparisons between a glass containing no lead and one containing 45 per cent. of lead.

**Winkelmann's Method of Observation.** The observations were made with the help of a telephone.

Two equal and parallel metal plates,  $P_1$   $P_2$ , face one another, and in the space intervening between their central portions there is a smaller metal plate  $Q$  parallel to them.

<sup>1</sup> The expansibility of the kinds of glass which are transparent to X rays is considerably less than that of platinum. There is, accordingly, a bad joint between the sealed-in wires and the glass. To prevent danger of the glass flying, the course of the wire should be straight, and its surface smooth. The joint can be made air-tight by a non-volatile oil.

<sup>2</sup> Results collected by Löwe, *Ann. d. Phys. u. Chem.*, 66. 401 (1898).

The glass plate to be tested is larger than  $Q$ , and of such thickness as to fit closely between  $Q$  and  $P_1$ . It can be inserted or removed at pleasure. The other plate,  $P_2$ , can be moved parallel to itself, to or from  $Q$ , through a measured distance.

When an observation is to be made,  $Q$  is connected with one of the secondary terminals of a small induction coil, the other terminal being earthed, and the two terminals of a telephone are connected with  $P_1$  and  $P_2$ . The effects in the telephone will be balanced so as to give a minimum of sound, when the condenser  $P_1Q$  (consisting of  $P_1$ , the side of  $Q$  facing it, and the intervening medium) has the same capacity as the condenser  $P_2Q$ .

Let  $d$  be the thickness of the glass plate, and  $K$  its permittivity. Then, before the introduction of the plate, the two distances will have the same value  $d$  when balance is obtained. When the glass is inserted, it will be necessary to move  $P_2$  nearer, by a certain amount  $x$ , to restore the balance, and  $K$  will be given by the equation

$$K = \frac{d}{d-x}.$$

In this way, Winkelmann investigated the permittivities of four specimens of glass, besides ebonite and paraffin, also of the liquids—benzol, petroleum, oil of turpentine, and alcohol. The glass plates, which had thicknesses varying from 3.07 mm. to 26.23 mm., showed the following permittivities :

Plate glass,	-	-	-	-	6.46
Plate glass,	-	-	-	-	7.57
Lead-free glass,	-	-	-	-	7.11
Glass with 45 per cent. lead,	-	-	-	-	7.44

The last two were discs for objectives, from the Jena Glass Works. In view of the small difference in their permittivities, with so large a difference in composition, Winkelmann renounced the idea of extending the test to other kinds of glass.

**Later Determinations.** H. Starke, by an adaptation of the method of Nernst, has recently determined the permittivities of ten different kinds of glass, and of a number of other solids.<sup>1</sup>

The alternate currents given by a small induction apparatus

<sup>1</sup> *Ann. d. Phys. u. Chem.*, 60, 629 (1897).

are sent through a Wheatstone's bridge, Fig. 29, whose four arms are liquid resistances  $r_1, r_2, r_3, r_4$ . Two condensers, of capacities

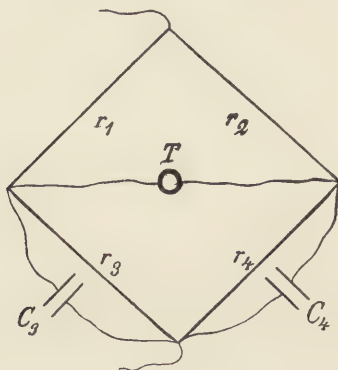


FIG. 29.

$C_3, C_4$ , are placed in parallel with the branches  $r_3, r_4$ . The conditions for balance in the telephone  $T$  can be shown<sup>1</sup> to be

$$\frac{r_1}{r_2} = \frac{r_3}{r_4} = \frac{C_4}{C_3}.$$

In order to make the capacities conform to this condition,  $C_3$  is varied by sliding a glass plate in or out through measured distances, the two metallic plates of the condenser being fixed.

<sup>1</sup> [To prove this, let  $i_1, i_2, i_3, i_4$  be the currents at any instant in  $r_1, r_2, r_3, r_4$ . When no current goes through the telephone  $T$ , the current into the first coating of  $C_3$  and out of the second, is  $i_1 - i_3$ .

For equality of potential at the two terminals of the telephone (or at the left and right corners of the diagram), we have the conditions

$$\begin{aligned} i_1 r_1 &= i_2 r_2, \\ i_3 r_3 &= i_4 r_4, \\ \frac{i_1 - i_3}{C_3} &= \frac{i_2 - i_4}{C_4}. \end{aligned}$$

Eliminating  $i_2$  and  $i_4$  from the 3rd equation by substitution from the other two, we get

$$\frac{i_3}{i_1} = \frac{\frac{C_4}{C_3} r_1 - r_2}{\frac{C_4}{C_3} - r_3}.$$

In order that the ratio of  $i_3$  to  $i_1$  may be variable, the second member must take the form  $\frac{0}{0}$ .



A liquid condenser, consisting of a shallow cylindrical vessel of nickel (in the first instance empty), with a collecting plate parallel to its base, is joined in parallel with the condenser  $C_4$ ; and  $C_3$  is then adjusted till balance is obtained in the telephone. The liquid condenser is then filled with purified benzol, which, according to Fl. Ratz<sup>1</sup> has, at temperature  $t^\circ$ , the permittivity

$$K_t = 2.2582 - .00164(t - 15).$$

Let  $x$  be the distance through which the slider in  $C_3$  must be moved to restore balance.

Now let the benzol be removed, and replaced by another liquid—say of permittivity  $K$ —and let the slider be moved through a further distance  $y$  till balance is restored. As equal movements of the slider produce equal changes of capacity, we have

$$\frac{K-1}{K_t-1} = \frac{x+y}{x},$$

which gives  $K$  in terms of  $K_t$  and measured distances. A liquid thus employed was ethylene-chloride, which, according to Landolt and Jahn,<sup>2</sup> has at  $0^\circ$  the permittivity 11.31.

If a glass plate introduced into the liquid of the condenser is found not to disturb the balance in the telephone, the inference is that the permittivity of the glass is the same as that of the liquid which it has displaced. By making a mixture of the two liquids above named, this result can be approximated to, and the slider can be adjusted till the balance is exact. Two mixtures, one of rather higher and the other of rather lower permittivity than the glass, will thus give the true value by interpolation.

One advantage of the method is that it can be carried out with small glass plates—say of 3 sq. cm. area. It is also independent of the shape of the plate and of the character of its surface. The limits of interpolation are widened, when the plate is a right cylinder or prism with its ends touching the two bounding plates of the liquid condenser.<sup>3</sup>

The following table gives Starke's results for the ten glasses;

<sup>1</sup> *Zeitschr. f. Phys. Chem.*, 19, 94 (1896).

<sup>2</sup> *Ibid.*, 10, 313 (1892).

<sup>3</sup> For the sources of error in the method we must refer to the original paper.

including permittivity  $K$ , specific gravity  $s$ , and the index of refraction for the  $D$  line :

Mark.	Description.	$K$	$s$	$K/s$	$n_D$
S. 186	Borate crown, - -	5.48	2.24	2.45	1.50936
O. 1948	Borosilicate crown,	6.20	2.47	2.48	1.51180
S. 169	Phosphate crown, -	6.39	2.58	2.51	1.52090
S. 4	Borate flint, - -	7.66	3.17	2.41	1.60305
O. 1610	Baryta crown, - -	7.81	3.21	2.43	1.57519
O. 1777	Baryta flint, - -	8.28	3.40	2.44	1.60284
O. 1922	Densest bar. crown,	8.40	3.55	2.37	1.60899
O. 1087	Silicate crown, -	7.20	2.54	2.83	1.51883
O. 1335	Dispersive crown, -	9.13	2.70	3.38	1.52333
O. 1469	Half flint, - - -	7.77	3.58	2.17	1.6129

Upon the whole, the order of arrangement for  $K$  is the same as for density, and also the same as for index of refraction ; but there are strongly marked exceptions.

**152. Electromagnetic Dispersion.** In connection with his investigation of the dielectric behaviour of glass, Winkelmann gives a list of previous determinations of the changes in  $K$  produced by changes in the frequency of alternation.<sup>1</sup> They all showed, in the case of glass, that  $K$  increases as the frequency diminishes. Since  $K$  corresponds, in Maxwell's theory, to the square of the index of refraction, this is opposite to the law of ordinary dispersion in the case of light, and may be regarded as coming under the head of "anomalous dispersion."

J. J. Thomson<sup>2</sup> found the value of  $K$  for a specimen of glass to be 2.7 when the oscillation-period was  $4 \times 10^{-7}$  of a second, and to be from 9 to 11 when it was that of an ordinary tuning fork.

Lecher,<sup>3</sup> in experiments on two glasses, obtained an opposite result. With a period  $3 \times 10^{-7}$  sec., the values of  $K$  were 7.3 and 6.5, and with a period of half a second, 4.7 and 4.6.

Blondlot,<sup>4</sup> by a comparison of glass with sulphur, obtained an indirect confirmation of the smallness of  $K$  for glass at high frequency. He deduced the value 2.8, which nearly agrees with J. J. Thomson's.

<sup>1</sup> *Ann. d. Phys. u. Chem.*, 38. 168 (1889).

<sup>2</sup> *Proc. Roy. Soc.*, 46. 292 (1889).

<sup>3</sup> *Ann. d. Phys. u. Chem.*, 42. 142 (1891).

<sup>4</sup> *Com. Ren.*, 112. 1058 (1891).

K. F. Löwe,<sup>1</sup> in a comprehensive experimental investigation, determined the magnitude and sense of the dielectric dispersion for a number of organic compounds, and for 10 different kinds of glass. He employed Starke's plan of mixing two liquids in such proportions that displacement of the mixture by a solid body does not disturb the electrical balance. In dealing with slow oscillations, he used the same two liquids as Starke, and tested the balance by Nernst's method. The glass plates introduced into the liquid had thicknesses of from .18 to .26 mm.

For rapid oscillations the liquids employed were benzol and acetone, with Drude's method of observation.<sup>2</sup> The glass plates were strips 4 mm. wide and 2 mm. thick. This method proved less exact than the other, and the final values were affected with an uncertainty of  $1\frac{1}{2}$  per cent.

In the following table the column headed  $K'$  contains Löwe's results for high frequency. His results for low frequency are given under the heading  $K$ , with Starke's results for nine glasses in an adjoining column. Löwe states that his glasses were similar to Starke's, except that he used the borosilicate S. 99 in place of

Mark.	Description.	$K$		$K'$
		Starke.	Löwe.	Löwe.
S. 196	Borate crown, - -	5.48	5.25	5.05
O. 2238	Borosilicate crown, -	6.20	6.20	6.15
S. 218	Phosphate crown, - -	6.39	6.40	6.20
O. 1580	Baryta crown, - -	7.81	7.83	7.65
O. 1353	Silicate flint, - -	8.28	8.29	7.30
O. 1993	Densest baryta crown, -	8.40	7.96	7.42
O. 1542	Silicate crown, - -	7.20	7.00	7.10
O. 2074	Dispersive crown, - -	9.13	9.14	7.70
O. 2051	Silicate flint, - -	7.77	7.78	7.62
S. 99	Borate flint, - - -	—	8.06	7.63

the borate flint S. 4. The trade numbers of the glasses are however different in the two lists, and it would therefore seem that the glasses were not exactly identical in kind. This may account for the difference in the case of densest baryta crown. With one doubtful exception, the high-frequency value  $K'$  is in

<sup>1</sup> *Ann. d. Phys. u. Chem.*, 66. 390 (1898).

<sup>2</sup> *Zeitschr. f. Phys. Chem.*, 23. 282 (1897).

every case smaller than the low-frequency value  $K$ . In the one exceptional case O. 1542, the difference in the opposite direction is within the limits of the errors of observation.

**153. Absorption of Electromagnetic Radiation.** For nine of the ten glasses, Löwe calculated the "coefficient of electric absorption"  $\kappa$ , defined by the rule that the amplitude of electric vibration diminishes in the ratio  $e^{-2\pi\kappa}$ , for each wave-length of advance in the dielectric.

Drude<sup>1</sup> has deduced, for the calculation of  $\kappa$ , the formulae

$$\kappa = \tan \frac{\phi}{2},$$

$\phi$  being an angle found from

$$\tan \phi = \frac{1}{K'} \sqrt{\{(K - K')(K' - n^2)\}},$$

$n$  denoting the index of refraction for luminous rays. The values thus calculated for  $\kappa$  are given in the second column of the following table. The third column contains the values, for the same glasses, of the optical characteristic  $\nu$  [which may conveniently be called the *constringence*], defined in Art. 17. Löwe calls attention to

Glass.	$\kappa$	$\nu$
S. 196	·11	60·4
O. 2238	·035	63·4
S. 218	·07	69·9
O. 1580	·06	56·9
O. 1353	·145	44·3
O. 1993	·11	56·4
O. 1542	—	58·5
O. 2074	·175	52·0
O. 2051	·06	36·8
S. 99	·09	42·5

the fact that the highly dispersive crown O. 2074 has the largest "electric absorption"; which is indicative (see Art. 24) of very high electric dispersion. A comparison of the values of  $\kappa$  and  $\nu$  brings out no obvious relation, beyond the fact that, for the three flint glasses,  $\kappa$  and  $\nu$  increase together.

<sup>1</sup>*Ann. d. Phys. u. Chem.*, 64. 131 (1889).



An attempt to determine by direct experiment the "electric absorption" of the glass O. 2074 was unsuccessful, and the above method of calculating  $\kappa$  needs verification.

**154. Verdet's Constant for Optical Glasses.** In an appendix to the description of a ring electromagnet, which gave a field of about 40 000 C.G.S. units of intensity, H. du Bois<sup>1</sup> has given the values of Verdet's constant for a number of Jena crown and flint glasses, found by examining them in this field. The glass plates employed were the identical plates previously used by Rubens in his measurement of absorption in the ultra red (see Art. 25). The glasses are the first nine in the list of Art. 23.

*Verdet's constant* for any substance may be defined as the amount of rotation of the plane of polarisation produced during the propagation of light from one point to another of the substance, when the magnetic potentials of the two points differ by one C.G.S. unit. If the rays of light are parallel to the lines of the field, the constant can be calculated by dividing the amount of rotation by the distance, and by the intensity of the field. The amount of rotation is usually expressed in minutes.

The last column of the following table, headed  $\omega_D$ , gives the values of Verdet's constant, in minutes, for sodium light, for the nine glasses, and also for fluorite. The order of arrangement is

Mark.	Description.	$n_D$	$\omega_D$
Fluorite		1.4340	0.0091
S. 204	Borate crown, - - -	1.51007	0.0163
O. 1092	Light baryta crown, - -	1.51698	0.0190
O. 1151	Dispersive silicate crown, -	1.52002	0.0234
S. 179	Medium phosphate crown, -	1.56207	0.0161
O. 1143	Dense barium silicate crown, -	1.57422	0.0220
O. 451	Light silicate flint, - - -	1.57524	0.0317
O. 469	Dense silicate flint, - - -	1.64985	0.0442
O. 500	Dense silicate flint, - - -	1.75130	0.0608
S. 163	Densest silicate flint, - -	1.88995	0.0888

according to the magnitude of the index of refraction for sodium light, whose values  $n_D$  are given in the preceding column. Both columns are for ordinary temperatures. Comparison between the

<sup>1</sup> *Ann. d. Phys. u. Chem.*, 51, 547 (1894).

two columns shows that, for the most part, the rotation increases with the index.

**Standard Plates for Measuring Magnetic Fields.** The rotation of the plane of polarisation, by a glass plate whose plane is perpendicular to the lines of the field, affords a convenient means of measuring the intensity of the field, especially if the glass be silvered at the back, so as to double the length of path and thereby double the rotation. The plate can be standardised beforehand, by observing its effect in a field of known intensity.

Zeiss supplies, for this purpose, standardised plates of the "densest silicate flint" S. 163. To avoid the confused mixing of multiple reflections which occurs with parallel plates, they are made (on the suggestion of H. du Bois)<sup>1</sup> slightly wedge-shaped, so that the disturbing images are thrown away from the principal image, and can be stopped out from the field of view of the analyser. If the diaphragm of the polariser does not subtend too large an angle as seen from the analyser, the angle of the wedge need not exceed 15' to 30'. A standardised glass about 1 mm. thick is suitable for fields of the order 1000 C.G.S. For weaker fields, thicker plates should be employed.

**155.<sup>2</sup> Another Investigation.** An investigation "on the electromagnetic rotation of the plane of polarisation in glasses, and its employment for measuring currents" has been recently published by O. Junghans (Zurich, 1902). The glasses were used in the form of cylinders about 5 cm. long and 1.5 cm. in diameter, with plane parallel ends, and, when under observation, occupied a definite position in the centre of a cylindrical coil traversed by a current. The rotation of the plane of polarisation was measured with a Wild's polaristrobometer. In the following table of results, the 9 glasses are arranged in descending order of their indices of refraction  $n_D$ , which is also the descending order of their values of Verdet's constant  $\omega_D$ . The first 6 are described as silicate flints, and the remaining 3 as barium silicates. The numbers I. to IX. are not the trade names, but mere reference numbers. As regards the other headings,  $i$  denotes the current, in amperes;  $R$  the rotation for sodium light, expressed in centesimal "grades";  $R'$  the quotient of  $R$  by  $i$ ;  $2l$  the length of the

<sup>1</sup>*l.c.* 548-549.

<sup>2</sup>Supplied by Dr. Hovestadt for this edition.

glass cylinder. Junghans does not carry his reductions beyond the computation of  $R'$ ; and the values of  $\omega_D$  given in the last column have been deduced by Dr. Hovestadt in the following way. The values of  $R'$  are in grades per ampere. To reduce to minutes per ampere, we must multiply by 54. Data given by Junghans show that the intensity of field for 1 ampere is 375 C.G.S. units. We have, accordingly,

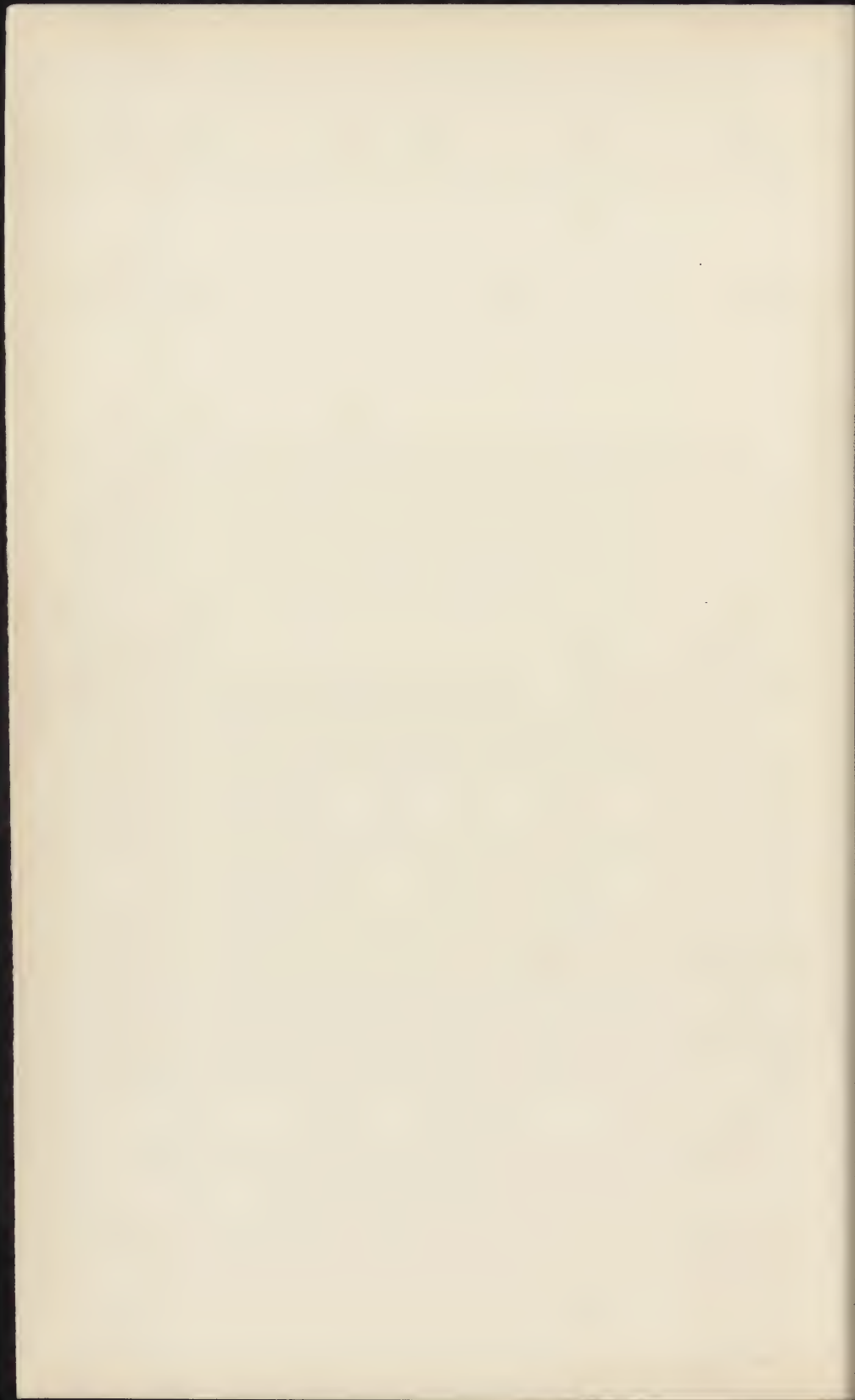
$$\omega_D = \frac{R' 54}{2l 375} = .144 \frac{R'}{2l};$$

which is the formula that has been employed. These values of  $\omega_D$  may be compared with those given in Art. 154. Junghans does not appear to have been acquainted with Du Bois' investigation.

Glass.	$n_D$	$i$	$R$	$R'$	$2l$ cm.	$\omega_D$
I.	1.9303	.6128	1°.827	2°.978	5.010	.0856
II.	1.7938	.6157	1.439	2.335	5.005	.0672
III.	1.7403	.6157	1.161	1.910	5.010	.0549
IV.	1.6797	.6116	.959	1.563	5.010	.0449
V.	1.6487	.6140	.810	1.317	4.982	.0381
VI.	1.6212	.6110	.747	1.224	4.982	.0354
VII.	1.6109	.6108	.466	.763	4.982	.0221
VIII.	1.5731	.6134	.462	.748	4.982	.0216
IX.	1.5398	.6100	.421	.683	4.982	.0197

Unsuccessful attempts were made to find a definite relation between the specific rotatory power of the 6 flint glasses, and their content of lead oxide. H. Becquerel's suggestion<sup>1</sup> that the rotatory power is proportional to  $n^2(n^2 - 1)$  gave deviations of  $\pm 4.33$  per cent. The supposition that the rotatory power is proportional to the square of the density, gave deviations of about  $\pm 3$  per cent.

<sup>1</sup> *Ann. de chim. et de phys.*, 5 Serie, t. XII.





## APPENDIX.

### REVISED LIST OF JENA OPTICAL GLASSES.

THE following list, issued January 1902, supersedes that given on pp. 26-31.

The phosphate and borate glasses are withdrawn, as they have been found wanting in durability.

The italics indicate glasses of decidedly new composition, first introduced at Jena.

The following are mentioned as specimens of ordinary silicate glasses for objectives :

Crowns	O. 144,	O. 60,	O. 203.	
Light flints	O. 340,	O. 318,	O. 569.	
Flints	O. 118,	O. 167,	O. 103,	O. 93.

They can be supplied in all sizes up to  $1\frac{1}{4}$  m. or more. Attention is called to the telescopic crown O. 2388, and the telescopic flint O. 2001, as almost completely abolishing the secondary spectrum.

Pressed lenses and prisms are supplied in the rough.

Coloured glasses of 18 kinds are specified.

Reference is made to separate catalogues for laboratory glass, thermometer tubing, water-gauge glasses, and lamp chimneys.

Trade No.	Description.	Index for <i>D</i> .	Mean Dispersion <i>C</i> to <i>F</i> .	$\nu = \frac{n-1}{\Delta}$ .
O. 82	<i>Borosilicate Crown</i> , - - - - -	1.4944	.00743	66.5
O. 2188	<i>Borosilicate Crown</i> , - - - - -	1.5013	.00760	65.9
O. 3258	<i>Crown of Lowest Index</i> , - - - - -	1.4782	.00726	65.9
O. 802	<i>Borosilicate Crown</i> , - - - - -	1.4967	.00765	64.9
O. 144	<i>Borosilicate Crown</i> , - - - - -	1.5100	.00797	64.0
O. 599	<i>Borosilicate Crown</i> , - - - - -	1.5069	.00813	62.3
O. 57	<i>Light Silicate Crown</i> , - - - - -	1.5086	.00823	61.8
O. 2388	<i>Telescope Crown</i> , <sup>1</sup> - - - - -	1.5254	.00852	61.7
O. 2122	<i>Heaviest Baryta Crown</i> , - - - - -	1.5899	.00970	60.8
O. 337	<i>Silicate Crown</i> , - - - - -	1.5144	.00847	60.7
O. 546	<i>Zinc Crown</i> , - - - - -	1.5170	.00859	60.2
O. 60	<i>Lime Silicate Crown</i> , - - - - -	1.5179	.00860	60.2
O. 138	<i>Silicate Crown of High Index</i> , - - - - -	1.5258	.00872	60.2
O. 567	<i>Silicate Crown</i> , - - - - -	1.5134	.00859	59.7
O. 227	<i>Barium Silicate Crown</i> , - - - - -	1.5399	.00909	59.4
O. 2118	<i>Crown of Low Index</i> , - - - - -	1.5095	.00858	59.4
O. 203	<i>Ordinary Silicate Crown</i> , - - - - -	1.5175	.00877	59.0
O. 2164	<i>Crown of Low Index</i> , - - - - -	1.5102	.00873	58.4
O. 2071	<i>Heaviest Baryta Crown</i> , - - - - -	1.6098	.01037	58.8
O. 15	<i>Zinc Silicate Crown</i> , - - - - -	1.5308	.00915	58.0
O. 211	<i>Heavy Barium Silicate Crown</i> , - - - - -	1.5726	.00995	57.5
O. 1209	<i>Heaviest Baryta Crown</i> , - - - - -	1.6112	.01068	57.2
O. 114	<i>Soft Silicate Crown</i> , - - - - -	1.5151	.00910	56.6
O. 1615	<i>Heaviest Baryta Crown</i> , - - - - -	1.6080	.01078	56.4
O. 2994	<i>Heaviest Baryta Crown</i> , - - - - -	1.6130	.01087	56.4
O. 463	<i>Baryta Light Flint</i> , - - - - -	1.5646	.01020	55.4

<sup>1</sup> Never quite free from bubbles and veins.

Trade No.	Partial Dispersions.			Ratios to $\Delta$ .			Density.
	$A'$ to $D$ .	$D$ to $F$ .	$F$ to $G'$ .	$\alpha$	$\beta$	$\gamma$	
O. 82	·00496	·00519	·00412	·667	·698	·554	2·33
O. 2188	·00498	·00533	·00424	·655	·701	·557	2·46
O. 3258	·00485	·00507	·00400	·668	·699	·552	2·23
O. 802	·00504	·00534	·00423	·659	·698	·553	2·38
O. 144	·00519	·00559	·00446	·651	·701	·559	2·47
O. 599	·00529	·00569	·00457	·651	·701	·562	2·48
O. 57	·00530	·00578	·00464	·643	·702	·564	2·46
O. 2388	·00549	·00602	·00484	·644	·707	·568	2·85
O. 2122	·00621	·00683	·00546	·640	·704	·563	3·32
O. 337	·00547	·00596	·00480	·645	·703	·567	2·60
O. 546	·00555	·00605	·00485	·646	·704	·565	2·59
O. 60	·00553	·00605	·00487	·643	·703	·566	2·49
O. 138	·00560	·00614	·00494	·642	·704	·566	2·53
O. 567	·00554	·00605	·00488	·645	·704	·569	2·51
O. 227	·00582	·00639	·00514	·640	·703	·566	2·73
O. 2118	·00557	·00604	·00491	·649	·704	·572	2·54
O. 203	·00563	·00616	·00499	·642	·702	·568	2·54
O. 2164	·00559	·00616	·00500	·640	·706	·573	2·54
O. 2071	·00665	·00730	·00590	·641	·704	·569	3·54
O. 15	·00587	·00644	·00520	·642	·704	·568	2·74
O. 211	·00630	·00702	·00568	·633	·706	·571	3·21
O. 1209	·00680	·00753	·00610	·636	·705	·571	3·55
O. 114	·00577	·00642	·00521	·634	·705	·572	2·55
O. 1615	·00685	·00761	·00617	·635	·706	·573	3·55
O. 2994	·00683	·00767	·00626	·629	·706	·576	3·60
O. 463	·00648	·00720	·00586	·635	·706	·575	3·11

Trade No.	Description.	Index for D.	Mean Dispersion C to F.	$\nu = \frac{n-1}{\Delta}$
O. 608	<i>Crown of High Dispersion,</i> - - -	1·5149	·00943	54·6
O. 722	<i>Baryta Light Flint,</i> - - -	1·5797	·01078	53·8
O. 846	<i>Baryta Light Flint,</i> - - -	1·5525	·01042	53·0
O. 602	<i>Baryta Light Flint,</i> - - -	1·5676	·01072	53·0
O. 2001	<i>Telescope Flint,</i> - - -	1·5211	·01007	51·8
O. 381	<i>Crown of High Dispersion,</i> - - -	1·5262	·01026	51·3
O. 583	<i>Baryta Light Flint,</i> - - -	1·5688	·01110	51·2
O. 152	Silicate Glass, - - -	1·5368	·01049	51·2
O. 543	<i>Baryta Light Flint,</i> - - -	1·5637	·01115	50·6
O. 527	<i>Baryta Light Flint,</i> - - -	1·5718	·01133	50·4
O. 164	<i>Borosilicate Flint,</i> - - -	1·5503	·01114	49·4
O. 2015	<i>Heaviest Baryta Crown of High Dispersion,</i>	1·6041	·01222	49·4
O. 575	<i>Baryta Light Flint,</i> - - -	1·5682	·01151	49·3
O. 522	<i>Baryta Light Flint,</i> - - -	1·5554	·01153	48·2
O. 726	Extra Light Flint, - - -	1·5398	·01142	47·3
O. 161	<i>Borosilicate Flint,</i> - - -	1·5676	·01216	46·7
O. 578	<i>Baryta Light Flint,</i> - - -	1·5825	·01255	46·4
O. 378	Extra Light Flint, - - -	1·5473	·01193	45·9
O. 364	<i>Borosilicate Flint,</i> - - -	1·5753	·01254	45·9
O. 1266	<i>Baryta Light Flint,</i> - - -	1·6042	·01381	43·8
O. 154	Light Silicate Flint, - - -	1·5710	·01327	43·0
O. 376	Ordinary Light Flint, - - -	1·5660	·01319	42·9
O. 276	<i>Ordinary Light Flint,</i> - - -	1·5800	·01373	42·2
O. 569	Ordinary Light Flint, - - -	1·5738	·01385	41·4
O. 340	Ordinary Light Flint, - - -	1·5774	·01396	41·4
O. 184	Light Silicate Flint, - - -	1·5900	·01438	41·1
O. 748	<i>Baryta Flint,</i> - - -	1·6235	·01599	39·1



Trade No.	Partial Dispersions.			Ratios to $\Delta$ .			Density.
	$A'$ to $D$ .	$D$ to $F$ .	$F$ to $G'$ .	$\alpha$	$\beta$	$\gamma$	
O. 608	·00595	·00666	·00543	·631	·706	·576	2·60
O. 722	·00681	·00761	·00621	·632	·707	·577	3·26
O. 846	·00657	·00736	·00602	·630	·707	·577	3·01
O. 602	·00675	·00759	·00618	·630	·708	·576	3·12
O. 2001	·00639	·00710	·00577	·635	·705	·573	2·50
O. 381	·00644	·00727	·00596	·629	·709	·582	2·70
O. 583	·00696	·00786	·00644	·627	·708	·580	3·16
O. 152	·00659	·00743	·00610	·628	·708	·582	2·76
O. 543	·00699	·00790	·00650	·627	·708	·583	3·11
O. 527	·00706	·00803	·00660	·623	·709	·582	3·19
O. 164	·00710	·00786	·00644	·637	·706	·578	2·81
O. 2015	·00763	·00867	·00712	·624	·709	·583	3·55
O. 575	·00718	·00817	·00672	·623	·710	·584	3·15
O. 522	·00718	·00819	·00677	·623	·710	·587	3·03
O. 726	·00711	·00810	·00669	·623	·709	·586	2·87
O. 161	·00762	·00860	·00709	·627	·707	·583	2·97
O. 578	·00777	·00891	·00739	·619	·710	·589	3·29
O. 378	·00739	·00847	·00705	·620	·710	·591	2·93
O. 364	·00787	·00888	·00735	·628	·708	·586	2·90
O. 1266	·00851	·00982	·00821	·616	·711	·594	3·50
O. 154	·00819	·00943	·00791	·617	·710	·596	3·16
O. 376	·00814	·00939	·00787	·617	·712	·596	3·12
O. 276	·00846	·00977	·00827	·616	·712	·602	3·22
O. 569	·00853	·00987	·00831	·615	·713	·600	3·22
O. 340	·00857	·00994	·00837	·614	·713	·600	3·21
O. 184	·00882	·01022	·00861	·613	·712	·597	3·28
O. 748	·00965	·01142	·00965	·605	·713	·604	3·67

Trade No.	Description.	Index for <i>D.</i>	Mean Dispersion <i>C</i> to <i>F.</i>	$\nu =$ $n - 1$ $\Delta$
O. 318	Ordinary Light Flint, - - - -	1·6031	·01575	38·3
O. 118	Ordinary Silicate Flint, - - - -	1·6129	·01660	36·9
O. 167	Ordinary Silicate Flint, - - - -	1·6169	·01691	36·5
O. 3269	<i>Heavy Baryta Flint</i> , - - - -	1·6570	·01809	36·3
O. 103	Ordinary Silicate Flint, - - - -	1·6202	·01709	36·2
O. 93	Ordinary Silicate Flint, - - - -	1·6245	·01743	35·8
O. 919	Ordinary Silicate Flint, - - - -	1·6315	·01770	35·7
O. 335	Heavy Silicate Flint, - - - -	1·6372	·01831	34·8
O. 102	Heavy Silicate Flint, - - - -	1·6489	·01919	33·8
O. 192	Heavy Silicate Flint, - - - -	1·6734	·02104	32·0
O. 41	Heavy Silicate Flint, - - - -	1·7174	·02434	29·5
O. 113	Heavy Silicate Flint, - - - -	1·7371	·02600	28·4
O. 165	Heavy Silicate Flint, - - - -	1·7541	·02743	27·5
O. 198	Very Heavy Silicate Flint, - - - -	1·7782	·02941	26·5
S. 228	<i>Heaviest Silicate Flint</i> , - - - -	1·9044	·04174	21·7

Trade No.	Partial Dispersions.			Ratios to $\Delta$ .			Density.
	$A'$ to $D$ .	$D$ to $F$ .	$F$ to $G'$ .	$\alpha$	$\beta$	$\gamma$	
O. 318	·00960	·01124	·00952	·609	·714	·605	3·48
O. 118	·01006	·01184	·01008	·606	·713	·607	3·58
O. 167	·01026	·01206	·01029	·606	·713	·608	3·60
O. 3269	·01093	·01295	·01106	·604	·716	·611	3·95
O. 103	·01034	·01220	·01041	·605	·714	·609	3·63
O. 93	·01053	·01243	·01063	·604	·715	·609	3·68
O. 919	·01063	·01266	·01085	·600	·715	·613	3·73
O. 335	·01099	·01308	·01124	·600	·714	·614	3·77
O. 102	·01152	·01372	·01180	·600	·714	·615	3·87
O. 192	·01255	·01507	·01302	·597	·717	·619	4·10
O. 41	·01439	·01749	·01521	·591	·718	·625	4·49
O. 113	·01526	·01870	·01632	·587	·719	·627	4·64
O. 165	·01607	·01974	·01730	·585	·720	·630	4·78
O. 198	·01719	·02120	·01868	·584	·721	·635	4·99
S. 228	·02394	·03023	·02726	·573	·724	·653	5·92

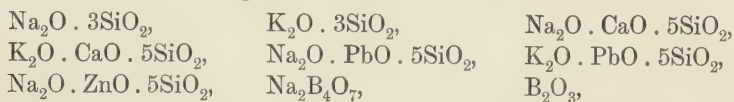
\* \* Sections A to H of the Appendix (together with Art. 155) have been specially prepared by Dr. Hovestadt for this edition.

### A. COLOURED GLASSES.

The persevering efforts which have been made at Jena to supply the long-felt want of ray-filters suited for various applications in science and art, are described in three communications.

- I. "The absorption of light in coloured glasses." By R. Zsigmondy. *Ann. d. Phys.* 4. 60 (1901).
- II. "Coloured glasses for scientific and technical purposes." By the same. *Zeitschr. f. Instrumen.*, 21. 97 (1901).
- III. "Jena light-filters." By C. Grebe. *Zeitschr. f. Instrumen.*, 21. (101) 1901.

In the first, Zsigmondy gives a very exact description of the light-absorption in several coloured glasses of definite composition, based on measurements made with a large spectro-photometer. The following types of composition were included:



and finally a lead silicate with 20 per cent.  $\text{SiO}_2$  and 80 per cent.  $\text{PbO}$ . Observations were also made on a soda borosilicate and a baryta borosilicate.

The proportions of colouring matter employed were respectively

Chrome oxide 1 per cent.,	Copper oxide 2 per cent.,
Cobalt oxide 0.1 per cent.,	Nickel oxide 0.25 per cent.,
Manganese oxide 1 per cent.,	Iron oxide 2 per cent.,
Uranium oxide 2 per cent.,	

of the mass of uncoloured glass.

The glasses were melted down in oxidising flames; then stirred, in the liquid condition, to get rid of streaks; then poured into moulds, and, after gradual cooling, cut into plates. The cut and polished plates were examined with a Glan spectro-photometer. The coefficients of extinction thus determined were used for the construction of representative curves, for which we must refer to the original memoir.

In his second communication, Zsigmondy describes the practical



results which have been attained at the Jena works. They are set forth in the following list of coloured glasses.

The last column gives the thicknesses of the plates which were examined; the examination being made with a Pulfrich comparison-spectroscope. The original gives also a graphical representation of each absorption spectrum, as seen in the instrument.

Trade No.	Designation.	Colour.	Spectral rays transmitted.	mm.
2728	Copper ruby glass	deep red	only red, to $\lambda=0.6\mu$ .	1.7
459 <sup>III</sup>	Gold ruby glass	red	red, yellow; and in thin layer, blue and violet.	
454 <sup>III</sup>	Uranium glass	bright yellow	red, yellow, green to $E_b$ ; and in thin layer, blue.	16
455 <sup>III</sup>	Uranium glass	bright yellow, strongly fluorescent		
440 <sup>III</sup>	Nickel glass	bright yellowish brown	red, yellow, weakened green, greatly weakened blue.	11
414 <sup>III</sup>	Chrome glass	yellowish green	yellowish green, almost like the Zettnow filter.	10
433 <sup>III</sup>	Chrome glass	greenish yellow	red to green, from $\lambda=.65\mu$ to $\lambda=.50\mu$ .	5
431 <sup>III</sup>	Green copper-glass	green	green, yellow, a little red and blue.	2.3
432 <sup>III</sup>	Chrome glass	yellowish green	yellowish green, a little red.	2.5
436 <sup>III</sup>	Copper-chrome glass	grass green	green.	5
437 <sup>III</sup>	Green filter	dark green	green; and in thin layer, blue.	5
438 <sup>III</sup>	Green filter	dark green	green.	5
2742	Copper glass	blue, like $\text{CuSO}_4$	green, blue, violet.	5-12
447 <sup>III</sup>	Blue violet glass	blue, like cobalt glass	blue, violet.	5
424 <sup>III</sup>	Cobalt glass	blue	blue, violet, extreme red.	4.5
450 <sup>III</sup>	Nickel glass	dark violet	violet $G-H$ , extreme red.	6
452 <sup>III</sup>	Violet glass	dark violet	violet $G-H$ slightly weakened; with dazzling illumination, extreme red.	7
444 <sup>II</sup>	Smoke gray glass	gray	whole spectrum weakened.	1-8
445 <sup>III</sup>	Smoke gray glass	gray	whole spectrum weakened.	1-3

These glasses can be used for the solution of various colour problems; for example:

Bipartite division of the spectrum, or its division into two complementary colours, can be effected in two ways:—I. By 2728 (deep red) and 2742 (blue, like copper sulphate). II. By 454<sup>III</sup> (bright yellow) and 447<sup>III</sup> (blue, like cobalt glass). The pair II. can be replaced by 433<sup>III</sup> (greenish yellow), and 424<sup>III</sup> (blue).

For the complementary pair I., the proper thicknesses are about  
2728, 1.6-1.7 mm.; 2742, 5 mm.

For the complementary pair II.

454<sup>III</sup>, 16 mm.; 447<sup>III</sup>, 1.5-2 mm.,

or 433<sup>III</sup>, 2.5-3.5 mm.; 424<sup>III</sup>, 3 mm.

Tripartite division of the spectrum into red, green, and blue (with violet), can be effected in various ways; for example by

2728, 1.7 mm.; 414<sup>III</sup>, 10 mm.; 447<sup>III</sup>, 1.5 mm.,

or by 2728, 1.7 mm.; 436<sup>III</sup>, 2.6 mm.; 447<sup>III</sup>, 1.8 mm.

Further information on three-colour selection is given below.

A fourfold division can only be imperfectly carried out. Up to the present, there is a want of a blue filter which will transmit the spectral blue alone and with sufficient brightness. Possibly 450<sup>III</sup> or 452<sup>III</sup> might serve for microphotography, and 447<sup>III</sup> for botanical purposes.

There is no glass transmitting only spectral yellow, and no purple glass absorbing only yellowish green.

Most of the Jena coloured glasses can be supplied to order; but the absorption bands vary somewhat in different meltings.

Grebe tested the sample glasses by means of a small spectrograph, using Cadett plates, sometimes with and sometimes without compensation. The following conclusions respecting glasses suitable for filters are selected from the results thus obtained.

The three glasses

2745, red; 438<sup>III</sup>, green; 447<sup>III</sup>, blue-violet

are specially suitable for the additive methods of three-colour projection. They correspond, with sufficient closeness, to Young's three elementary colour-sensations.

The glasses of a second group,

Putzler<sup>1</sup>, reddish orange; 438<sup>III</sup>, green; 447<sup>III</sup>, blue-violet  
+ complement + complement

are conspicuously fitted for the panchromatic process.

<sup>1</sup> A glass easily obtainable, made by Putzler of Dantzig.

Their transmission curves closely resemble the curves of distribution of the three elementary sensations in the spectrum.

Lastly, the three glasses

423<sup>m</sup>, bright blue ; 459<sup>m</sup>, purple ; 454<sup>m</sup>, yellow ;

taken in order, are very nearly the complements of the three last named. They represent the ideal colours for three-colour printing, and for subtractive synthesis. By means of these three glasses combined subtractively, Grebe has obtained a nearly perfect reproduction of the prismatic spectrum (the "three-colour-glass spectrum").

### B. OPAL GLASS.

Some data respecting Jena opal glass [milchglas] have been published by Schott and Herschkowitz.<sup>1</sup>

The purpose of the usual external globes, whether of opal glass, roughened glass, or etched glass, is to produce an advantageous distribution of the light. The ideal of such a diffusely distributing glass would be attained if absorption were quite abolished, and all the light were scattered and transmitted in about equal proportions. The absorption which actually occurs is due, in the case of opal glasses, to the fact that the separated particles which scatter the light are only imperfectly transparent. Theoretically, there is no difficulty in imagining this function to be discharged by perfectly transparent particles. It would suffice that these particles had a different index from the material in which they were embedded. For some time past, the Jena works have been producing an opal glass which comes much nearer to this ideal than those hitherto obtainable. A thin section of this new glass shows, under the microscope, a glassy bodyground through which numerous closely lying separate transparent spheres are scattered.

No information is given as to its composition and manufacture. Photometric comparisons of it with ordinary opal glass have shown that the absorption of light is reduced, in the most unfavourable cases, to one half, and in most cases to one fourth, of its ordinary amount.

<sup>1</sup>"On the distribution of incandescent gaslight in space, and the effective employment of opal glass in illumination"—*Jour. f. Gasbeleuchtung und Wasserversorgung*, 1901, Heft 26.

In discussing the best form for a lamp shade, an ordinary incandescent gaslight cannot be treated as a point source. If it is centrally placed within a large globe, the different zones of the globe will receive unequal illuminations. Schott and Herschkowitz have determined photometrically the distribution of the light for successive zones, each of  $10^\circ$ , commencing from the equator; and their paper (which is fully illustrated) shows how this knowledge may be applied (with the help of the new opal glass) to render the distribution as effective as possible. The *autosit* shades made by Schott and Co. are intended for this purpose.

### C. DURAX GLASS FOR GAUGE TUBES.

(See p. 227.)

A new glass for water-gauge tubes for steam boilers has recently been made at the Jena Works, and commercially introduced under the designation *Durax Glass*. As regards its composition, no information is given beyond the fact that it is a borosilicate. Recent advances in the production of iron and steel of high and uniform tenacity have led to the use of much higher pressures of steam, with a corresponding gain in efficiency; and the requirements for strength in gauge-tubes have accordingly become more severe. An experimental investigation conducted by O. Schott and M. Herschkowitsch<sup>1</sup> has furnished definite information as to the relative merits of the various kinds of gauge-tube glass at present in use, as compared with one another, and more especially as compared with *Durax* glass. The tubes tested included French, English or Scotch, Jena compound, melting, combustion, and *Durax* tubes. The external diameters were 18–20 mm., and the thicknesses 2–3.5 mm. The following were the main results.

All kinds, when cold, were able to withstand very high internal pressure (170 to 333 atmospheres).

The use of hot water and steam, without external chilling, diminished the resisting power of all tubes by from 35 to 40 atmospheres. The comparisons up to this point showed no superiority of one glass to another in any respect.

<sup>1</sup>“On water-gauge tubes and their protecting glasses,” *Zeitschr. d. Vereins deutscher Ingenieure*, 45 (1901). The methods employed could scarcely be made intelligible without the illustrations which the paper contains.



Great differences, however, appeared when the tubes, under the internal pressure of hot water and steam (as in actual use) were exposed externally for one second to a continuous stream of cold water drops. For example, in one series of experiments, the following were the pressures at which the tubes gave way :

French.	English.	Compound.	Combustion.	Durax.
6	7	15	24	27 atmospheres.

The Durax tubes here show a distinct superiority to any of the others. And it is a well-known fact that in practice many breakages occur from accidental external cooling by drafts of cold air, sprinkling of water, rain-drops, or snow-flakes.

The corroding action of water and steam, at high temperatures, on the surface of glass, was much less noticeable in Durax than in the other glasses, *provided that the water did not contain an excessive amount of free alkali.*

#### D. DEPRESSION OF ZERO OF THERMOMETER BY HEATING.

(See p. 255.)

W. Schloesser,<sup>1</sup> in comparing thermometers belonging to the "Standards Commission" with thermometers of *verre dur* whose errors had been determined at the *Bureau International*, observed the depressions produced by heating to temperatures between 10° and 90° for eight thermometers of 16<sup>III</sup>, and ten of *verre dur*. His results, when reduced to the form

$$E_0 - E_t = pt + qt^2 \quad (\text{see p. 255}),$$

give the following values of the two constants  $p$ ,  $q$ , and of the "depression-constant"  $D$  :

	$10^5 p$	$10^5 q$	$D$
Normal-Glass 16 <sup>III</sup>	5.2	0.655	0.071
<i>Verre dur</i>	55.35	0.6875	0.124

Comparing these with the values given at pp. 255, 256, one is struck with the smallness of  $p$  and the largeness of  $q$ , which (especially in the case of 16<sup>III</sup>) deprive the depression-curve of all likeness to a straight line. The working out of the formula between 0° and 100°, with the values assigned by the three different observers, is

<sup>1</sup> *Zeitschr. f. Instrum.*, 21. 281 (1901).

exhibited in the following table. The discrepancies are not yet explained.

Temp.	Normal-glass 16 <sup>III</sup> .			<i>Verre dur.</i>		
	Böttcher.	Thiesen.	Schloesser.	Guillaume.	Thieson.	Schloesser.
0°	0	0	0	0	0	0
10	7	7	1	9	10	6
20	14	14	4	18	20	14
30	21	22	7	28	31	23
40	27	31	13	37	42	33
50	33	40	19	47	52	45
60	40	50	27	57	64	58
70	46	61	36	67	75	72
80	52	72	46	78	86	88
90	57	83	58	89	98	105
100	63	96	71	100	110	124

#### E. REDUCTION OF MERCURY THERMOMETERS OF 16<sup>III</sup> AND 59<sup>III</sup> TO THE HYDROGEN SCALE.

(See p. 299.)

The introduction of the hydrogen scale into practical thermometry, has given great importance to the reduction tables of Art. 123. Every step towards their completion, and every contribution throwing light on the degree of their exactness, is therefore of interest.

*Thermometers of Normal-Glass 16<sup>III</sup>.*—W. Schloesser conducted an investigation<sup>1</sup> (see *D*) having for its object to compare a large number of thermometers belonging to the Standards-Commission, made of different German glasses, with the hydrogen scale, by intermediate comparisons with thermometers of *verre dur*. We will first give the results obtained for 10 thermometers of 16<sup>III</sup>.

This was the first comparison ever made between thermometers of these two glasses at temperatures below freezing; and a special apparatus was employed, of which the author gives a description with illustrations. The observations extended from  $-20^{\circ}$  to  $+90^{\circ}$ , and the formula deduced from them was

$$t_r - t_{16} = 10^{-9} \times 172 (100 - t_{16}) t_{16} - 10^{-10} \times 656 (100 - t_{16})^2 t_{16},$$

the symbols having the same meanings as in Art. 123 (p. 298).

<sup>1</sup> *Zeitschr. f. Instrum.*, 21. 281 (1901).

The values computed by this formula are given under the heading "calculated" in the third column of the following table, the corresponding observed values being given in the second column. The fourth column gives, for comparison, the results obtained by Thiesen, Scheel and Sell (see p. 278); and the differences (Thiesen - Schloesser) are shown in column 5.

VALUES OF  $t_T - t_{16}$ ; UNIT  $0^{\circ}.0001$ .

Temp.	Schloesser.		Thiesen.	Diff.
	Obs.	Calc.		
-25°	+265	+251		
-20	+197	+185		
-15	+153	+127		
-10	+110	+77		
-5	+45	+35		
+10	-17	-52	-47	+5
+20	-50	-81	-83	-2
+30	-96	-93	-109	-16
+40	-68	-90	-124	-34
+50	-73	-78	-129	-51
+60	-89	-59	-124	-65
+70	-26	-38	-109	-71
+80	-28	-18	-83	-65
+90	-42	-4	-47	-43

The elaborate attempts which were made to explain this discrepancy led to no definite result; and the agreement was not improved by leaving out of account Schloesser's observations below  $0^{\circ}$ . A partial explanation is furnished by the differences which notoriously exist between individual instruments of the same kind of glass. Irregularities arising from this source can only be eliminated by the use of large numbers of thermometers of both kinds; and it is to be noted that Schloesser used ten thermometers of "normal glass," and eight of *verre dur*; whereas the other observers used only three of each kind.

By adopting Chappuis' reductions of Tonnelot thermometers to the hydrogen scale, Schloesser finally obtained the results given in the third column of the following table, which also contains Thiesen's results, for comparison. ( $t_H$  denotes temperature by Hydrogen scale).

VALUES OF  $t_{16} - t_H$ ; UNIT  $0^{\circ}\cdot001$ .

Temp.	Thiesen.	Schloesser.	Diff.
10°	56	57	1
20	93	93	0
30	113	112	-1
40	120	116	-4
50	116	110	-6
60	103	96	-7
70	83	76	-7
80	58	52	-6
90	30	26	-4

In Art. 123 it was necessary to employ extrapolation for reducing  $t_{16}$  to the hydrogen scale at temperatures below freezing. It is of interest to compare these provisional determinations (p. 300) with the determinations which can now be derived from direct comparisons of  $t_{16}$  with  $t_H$  at these temperatures.

VALUES OF  $t_H - t_{16}$ .

	Schloesser.	Extrapolation.
-25°	$0^{\circ}\cdot258$	$0^{\circ}\cdot25$
-20	$\cdot191$	$\cdot19$
-15	$\cdot132$	$\cdot13$
-10	$\cdot081$	$\cdot08$
- 5	$\cdot037$	$\cdot04$

The difference in no case exceeds  $0^{\circ}\cdot01$ .

*Thermometers of the borosilicate 59<sup>III</sup>.* No direct comparisons of thermometers of this glass are available, but indirect comparisons with the hydrogen scale can be made in the following way.

Grützmaker<sup>1</sup> has calculated for each degree from  $0^{\circ}$  to  $300^{\circ}$  by Wiebe and Böttcher's reduction formula (p. 281) the difference between the air thermometer and the "normal-glass" thermometer. These differences we shall now denote by  $t_L - t_{16}$ . By adding these to the values of  $t_{16} - t_H$  calculated by Scheel (see p. 298), he obtains the

<sup>1</sup> *Zeitschr. f. Glasinstrum.-Industrie*, 5. 108 (1896). The reductions are reproduced by Grützmaker in *Ann. d. Phys. u. Chem.*, 68. 769 (1899).



values<sup>1</sup> of  $t_L - t_H$ . By adding these to Grützmacher's determinations of  $t_{59} - t_L$  (see table, p. 287), values of  $t_{59} - t_H$  are obtained, which may be used to check Scheel's values given on p. 300. We content ourselves with giving the results for every tenth degree.

UNIT 0°:001.

Temp.	$t_L - t_{16}$	$t_{16} - t_H$	$t_L - t_H$	$t_{59} - t_L$	$t_{59} - t_H$	Scheel. $t_{59} - t_H$	Diff.
10°	- 49	56	7	17	24	24	0
20	- 83	93	10	26	36	35	1
30	- 103	113	10	29	39	38	1
40	- 110	120	10	26	36	34	2
50	- 107	116	9	21	30	26	4
60	- 96	103	7	14	21	16	5
70	- 78	83	5	6	11	8	3
80	- 54	58	4	1	5	1	4
90	- 28	30	2	-2	0	-2	2

The differences have all the same sign, but their maximum amount is only 0°:005.

*Other reductions to the hydrogen scale.* Twelve old thermometer glasses, including seven Jena glasses, were compared with the hydrogen thermometer by Grützmacher<sup>2</sup> at the Reichsanstalt. The 12 thermometers were compared with four chief standards of 16<sup>III</sup>, which had already been compared with the air thermometer, and could thus, by Grützmacher's values of  $t_L - t_H$ , be compared with the hydrogen thermometer. Reductions to the hydrogen thermometer were thus computed for the 12 old glasses. Most of these glasses have been superseded, or have never been in practical use.

Schloesser, in the investigation quoted above, also gives comparisons of several old (Jena and other) thermometer glasses with the hydrogen scale, derived from direct comparisons by himself with Tonnelot thermometers.

<sup>1</sup> The values from 0° to 100° are given for each degree to furnish the means of reducing to the hydrogen thermometer the various reductions to the air thermometer published by the Reichsanstalt down to Oct. 1896. Since that date the Reichsanstalt has reduced temperatures between 0° and 100° to the hydrogen thermometer.

<sup>2</sup> *Dissertation*, Berlin, 1900.

## F. INFLUENCE OF TEMPERATURE ON THERMAL CONDUCTIVITY.

The *Influence of Temperature on the Conductivity of Glass* has been specially examined by J. Krüger,<sup>1</sup> mainly with the view of testing the correctness of Winkelmann's conjecture (see p. 212) as to the cause of the differences between Paalhorn's and Focke's results. Krüger used the identical apparatus which had been employed by Paalhorn; an apparatus containing (as described in Art. 92) a conducting column composed of three copper and two glass plates; but the two glass plates were now of the same glass at different temperatures. In the course of his research, he introduced a modification consisting in alternate reversals of the direction of the flow of heat through the conducting column, observations with the flow in opposite directions being combined in pairs; and his final results were deduced from observations so combined.

The reductions were directed to finding the value of the temperature-coefficient  $\alpha$  defined by

$$K_t = K_0 (1 + \alpha t);$$

and the values found for  $\alpha$  were so small that little could be done beyond determining their signs. No attempt was therefore made to examine the influence of chemical composition; and the experiments were limited to three glasses, O. 137, S. 226, and O. 709. The first is identical with No. 83 of Winkelmann's list (p. 145), the second is nearly identical with No. 69, and the third with No. 25. The values found for  $\alpha$  were

O. 137	S. 226	O. 709
$10^5 \alpha = -(31 \pm 15),$	$-(34 \pm 1),$	$-(45 \pm 13).$

The conductivity accordingly (as in the case of most solid bodies) diminishes slightly as the temperature increases; the difference per degree amounting to only about .03 or .05 per cent. These coefficients do not correspond either in magnitude or in sign with the view that the difference between Paalhorn's and Focke's results is to be explained by them.

After discussing the circumstances, Krüger comes to the conclusion that the differences in question are probably due to small differences in the chemical composition of nominally identical glasses.

<sup>1</sup> *Inaugural Dissertation, Jena, 1901.*

## G. DECOMPOSITION BY AIR AND DUST.

(See Chap. X.)

Observations on the *decomposition of different glasses when exposed to air and dust*, have been published by E. Zschimmer.<sup>1</sup> They were made upon about 200 pieces of glass with polished plane surfaces, which, with the view of testing the *durability, in ordinary conditions*, of glasses destined for optical use, had been stored in Jena for several years in a dry place, and enclosed in a way which only imperfectly excluded air.

A close connection was found (as might have been expected) between the chemical composition of the glasses and their susceptibility to decomposition under the influence of air and dust, the following being the most important conclusions.

The behaviour of *Silicates without lead* depends almost entirely on their content of alkali. Even with as little as 10 per cent., they exhibit, under the microscope, the so-called *dusty disintegration*; that is to say, the minute particles of dust which fall on the surface become centres of decomposition, the character of the decomposition being different according to the composition of the glass.

When the proportion of alkali is increased beyond 10 per cent., the transition is soon made to *homogeneous decomposition*, which attacks the whole surface uniformly.

With 20 per cent. of alkali, the deposit on the surface is visible to the naked eye; and larger proportions give rise to coarser phenomena—the formation of drops, and the crystallisation of carbonates. Deliquescent carbonate of potash covers the surface with more or less minute drops; whereas carbonate of soda, being only slightly hygroscopic, covers it with assemblages of crystals. Whether lime, and zinc oxide, have a material influence on these phenomena, is not definitely known. Baryta, when present in considerable quantity, promotes the dusty disintegration.

*Lead silicate* glasses showed dusty decomposition in the form of what are known as *lead-spots*. They were not seen till the lead oxide amounted to 20 per cent.; and with increasing percentages they became more and more prominent. Lead-spots are a phenomenon well known to opticians in the case of flint glasses. The spots were brown, or blue-black, and showed (under the microscope), in the centre of each, the

<sup>1</sup> *Chemiker Zeitung*, 1901. 25. No. 69.

exciting particle of dust, surrounded by scaly leaf-like products of decomposition, forming a black or brown mass. A similar appearance can be produced, in glasses rich in lead, by immersing them in a concentrated solution of grape sugar. After the lapse of a few days, they develop spots with a bluish-brown shimmer, which remain after washing and gentle wiping. Presumably it is a case of the formation of lead mirrors by reduction. In lead silicates containing alkali, the separation of alkali at the surface is promoted by the presence of the lead, if in sufficient amount.

The *borate* glasses without lead behave in a manner easily understood. Pure boric acid, after fusion, and most of its salts, absorb from the air considerable quantities of water, while continuing to exhibit a dry surface. Glass rich in boric acid behaves in the same way; it swells, while remaining dry; and no change in the surface is noticeable till the quantity of moisture absorbed becomes excessive; when the surface begins to split. The bursting of the surface can be produced at an earlier stage by heating the glass. In the case of a glass with 60 per cent. of  $B_2O_3$ , this action was so strong that the whole surface broke up into splinters when heated. Another glass, with 50 per cent.  $B_2O_3$ , began to show microscopic cracks when heated to  $150^\circ$ . A borosilicate with 22 per cent. showed no change in its surface even after heating. Percentages of from 30 to 40 of  $B_2O_3$  may be regarded as consistent with durability.

*Lead borates* exhibit decomposition of the surface as soon as the amount of lead oxide reaches 20 per cent.; the effect showing itself by iridescence, the colours changing with the angle of incidence of the light. Heating deepens the colouring, but there is no flaking off; and polishing the surface increases the brilliancy of the display of colour. The glass must therefore be affected to a considerable depth.

The *phosphate* glasses are all hygroscopic; and their changes of surface resemble those of the alkali silicates; but are easily distinguished from these, under the microscope, by the characteristic property of the separation of crystals.

#### H. OPTICAL EFFECTS OF STRESS.

The *change of optical properties produced by elastic deformation* has been investigated for various glasses by F. Pockels.<sup>1</sup> His investiga-

<sup>1</sup> *Ann. d. Phys.*, Ser. 4, Vol. 7, 745 (1902).



tions were directed to the determination of the two coefficients  $p, q$  in the equations

$$\omega_x = \omega + qx_x + py_y + pz_z,$$

$$\omega_y = \omega + px_x + qy_y + pz_z,$$

$$\omega_z = \omega + px_x + py_y + qz_z,$$

employed by F. Neumann for expressing the influence of elastic deformation on the propagation of light in isotropic substances;

$x_x, y_y, z_z$  denoting the three principal dilatations;

$\omega$  the velocity of propagation in the absence of stress;

$\omega_x, \omega_y, \omega_z$  the three principal velocities of propagation in the stressed substance.<sup>1</sup>

The axes of  $x, y, z$  are so chosen as to coincide with the directions of the three principal dilatations. They will be the principal axes of the wave-surface.

Taking  $E$  (as in Chap. VII.) to denote Young's modulus, and  $\mu$  Poisson's ratio, a thrust  $Z_z$  in the direction of  $z$  will produce the three principal dilatations,  $z_z = -Z_z/E$ ,  $x_x = y_y = \mu Z_z/E$ ; and  $p$  and  $q$  can be deduced from measurements of  $\omega_z - \omega$  and  $\omega_x - \omega$ , or one of these quantities and the difference of the two. Their values will be different for different wave-lengths.

Rectangular plates, about 20 mm. long, 7 mm. wide, and 5 mm. thick, of the glasses to be tested, were ground at Zeiss' works, in pairs or in sets of four. The  $20 \times 7$  faces were ground accurately plane and parallel, and finely polished. In each experiment, one of these plates, with its greatest dimension vertical, was subjected to vertical pressure applied by a steel lever.

Observations were first made with a Jamin's interferential refractor, to determine the absolute retardation, introduced by the compression, in the wave polarised perpendicular to the direction of pressure; and then, secondly, with a Babinet's compensator, to determine the relative retardation of the two waves propagated perpendicular to the polished faces. These determinations furnish the means of calculating  $p/\omega$  and  $q/\omega$ .

Seven glasses were tested, and particulars respecting them are given in the following table. The first column contains their trade numbers; the second column, headed  $W$ , their numbers in Winkelmann's list (pp. 145-147);  $s$  is specific gravity;  $E$  Young's modulus;

<sup>1</sup>[Pockels calls them "the velocities of the waves polarised perpendicular to the  $x, y$ , and  $z$  axes."

$\mu$  Poisson's ratio;  $3a$  the cubic coefficient of expansion;  $n$  the index of refraction for sodium light.

The values of  $E$  and  $\mu$  for the glass O. 428 were not directly observed, but computed from chemical composition.

Glass O. 2154 is nearly identical in composition with Winkelmann's 86, and O. 500 with 50.

Trade No.	$W$ .	$s$ .	$E$ .	$\mu$ .	$3a \cdot 10^7$ .	$n$ .
S. 205	2=22	2.243	4800	0.274	202	1.5075
O. 428	42	2.457	4720	0.268	—	1.5123
O. 658	21	2.758	5470	0.250	157	1.5452
O. 2154	47	3.115	6100	0.222	—	1.5700
O. 1571	26	3.88	5470	0.224	—	1.6440
O. 500	33	4.731	5500	0.239	241	1.7510
S. 57	20	6.335	5035	0.261	280	1.9625

The results of the investigation (for sodium light) are given in the following table; in which  $v$  denotes  $n\omega$  the velocity in vacuo.

	S. 205.	O. 428.	O. 658.	O. 2154.	O. 1571.	O. 500.	S. 57.
$\frac{p}{\omega}$	.274	.0908	.289	.306	.335	.354	.427
$\frac{q}{\omega}$	.166	.0228	.182	.213	.264	.319	.466
$\frac{p}{v}$	.182	.060	.187	.195	.204	.202	.218
$\frac{q}{v}$	.110	.015	.118	.135	.160	.182	.237

By means of the equations

$$\frac{\omega_x - \omega}{\omega} = \frac{n - n_x}{n} = \frac{q}{\omega} x_x + \frac{p}{\omega} (y_y + z_z),$$

the values of  $p/\omega$  and  $q/\omega$  serve to determine the changes of the index of refraction.

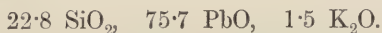
The glasses are arranged in ascending order of  $s$  and of  $n$ . If we leave out of account O. 428, for which the values of  $E$  and  $\mu$  were only determined by a doubtful calculation, all the four quantities  $\frac{p}{\omega}$ ,  $\frac{q}{\omega}$ ,  $\frac{p}{v}$ ,  $\frac{q}{v}$ , increase with  $s$  and  $n$  from each column to

the next, the increase being more rapid for  $\frac{q}{\omega}$  and  $\frac{q}{v}$  than for  $\frac{p}{\omega}$  and  $\frac{p}{v}$ ; but along with this increase there is a diminution of the difference between  $\frac{p}{\omega}$  and  $\frac{q}{\omega}$ , and, therefore, of the difference between  $p$  and  $q$ .

$p$  is greater than  $q$  in all light glasses, and also in the heavy flint O. 500; the double refraction in these is accordingly negative. In the heaviest flint S. 57,  $q$  is greater than  $p$ ; that is, thrust in this glass produces positive double refraction. This is a result never before observed in an amorphous substance.

As O. 500 and S. 57 are both of them lead silicates, Pockels inferred that there must be some intermediate lead silicate for which  $p$  and  $q$  are equal, so that it would remain singly refracting under thrust in any one direction, and therefore under any distortion whatever within its elastic limits.

In endeavouring to determine by graphical interpolation the composition which would give this result, the four glasses S. 57, O. 500, O. 1571, O. 2154 were taken into account, and the composition indicated was



An experimental melting of about this composition was made at the Jena Works, and, when tested with sodium light, was found to give positive double refraction having only  $\frac{1}{16}$  the magnitude of that given by S. 57. Pockels concludes that a diminution of 0.6 in the PbO would make the double refraction vanish.

Besides sodium light, the glasses were also tried with lithium light and thallium light. Observations were fewer than with sodium light, and therefore the same degree of precision cannot be claimed for the results. They served, however, to show that the chromatic dispersion of the double refraction is mostly very small, and may have either sign. It is only considerable in the heaviest flint glasses.

The change of index produced by compression or dilatation uniform in all directions can be calculated from the values found for  $p/\omega$  and  $q/\omega$ . Calling the cubic dilatation  $\delta$ , we have

$$x_x = y_y = z_z = \frac{1}{3}\delta,$$

$$\frac{\omega_x - \omega}{\omega} = \left( \frac{2p}{\omega} + \frac{q}{\omega} \right) \frac{\delta}{3} = \frac{d\omega}{\omega} = - \frac{dn}{n};$$

also

$$\delta = - \frac{ds}{s},$$

whence

$$\left( \frac{2p}{\omega} + \frac{q}{\omega} \right) \frac{n}{3} = - \frac{dn}{\delta} = s \frac{dn}{ds}.$$

We thus find for the seven glasses

	S. 205	O. 428	O. 658	O. 2154	O. 1571	O. 500	S. 57
$s \frac{dn}{ds} =$	·358	·106	·392	·485	·512	·600	·865

If we assume any one of the three formulae on p. 61 (for the "constant of refraction") as remaining constant during uniform compression, the assumption will give  $s \frac{dn}{ds}$  as a function of  $n$ . Pockels tested all three formulae in this way, and found that the second (which makes  $n^2 - 1$  proportional to the density) gave fair results for some of the glasses, but bad results for others. The first and third formulae (especially the third) gave much worse results. In connection with this question, it is to be noted, as an obvious inference from the above values of  $s \frac{dn}{ds}$  for the seven glasses, that the change of index with uniform compression, whether measured by  $s \frac{dn}{ds}$  or by  $\frac{s}{n} \frac{dn}{ds}$ , increases rapidly with the original density and index.

By the *pure temperature coefficient of index* is meant the whole value of  $\frac{dn}{dt}$  minus the part due to mere change of density. Using the symbol  $\partial$  for partial and  $d$  for total differentiation, we have, accordingly,

$$\frac{\partial n}{\partial t} = \frac{dn}{dt} - \frac{\partial n}{\partial s} \frac{ds}{dt} = \frac{dn}{dt} + 3as \frac{\partial n}{\partial s}$$

as the formula for computing the "pure temperature coefficient"  $\partial n / \partial t$ .

Pulfrich's observations (partly given at p. 59) led to the values:

	S. 205	O. 658	O. 500	S. 57
$10^5 \frac{dn}{dt} =$	-·074	+·299	+·775	+1·45
$10^5 \frac{\partial n}{\partial t} =$	+·65	+·914	+2·22	+3·87

The pure temperature coefficient of index in these glasses,  $\frac{\partial n}{\partial t}$ , is thus always positive, and increases very rapidly with the content of lead; this increase being probably due to the increase of absorption in the ultra-violet with increasing temperature (p. 62). As a further test of the correctness of this explanation, Pockels calculated  $\frac{\partial n}{\partial t}$  for lithium light and thallium light, using Pulfrich's values of  $\frac{dn}{dt}$  (with the aid of interpolation) and his own values of  $s \frac{\partial n}{\partial s}$ .



The following are the results :

	S. 205	O. 658	O. 500	S. 57
$10^5 \frac{dn}{dt} \left\{ \begin{array}{l} \text{Li} \\ \text{Tl} \end{array} \right.$	$-.064$ $-.055$	$.261$ $.33$	$.685$ $.90$	$1.16$ $1.73$
$s \frac{\partial n}{\partial t} \left\{ \begin{array}{l} \text{Li} \\ \text{Tl} \end{array} \right.$	$.374$ $.339$	$.411$ $.376$	$.602$ $.596$	$.879$ $.829$
$10^5 \frac{\partial n}{\partial t} \left\{ \begin{array}{l} \text{Li} \\ \text{Tl} \end{array} \right.$	$.69$ $.63$	$.906$ $.920$	$2.13$ $2.34$	$3.62$ $4.05$
Diff.	$-.06$	$.014$	$.21$	$.43$

They bear out the explanation, except in the case of the borate crown S. 205, which shows a diminution of the temperature coefficient with decrease of wave length. This is opposite to what we should expect from increase of ultra-violet absorption, and suggests rather a displacement of the ultra-red absorption bands in the case of this glass.

## NOTES BY THE SENIOR TRANSLATOR.

(a) ON THE NAME TO BE GIVEN TO THE QUALITY REPRESENTED  
BY ABBE'S SYMBOL  $\nu$ . (See page 24.)

The quality in question is a tendency to hold together the rays of different colours, so as to make dispersion small; and I propose that it be denoted by the name *constringence*, which literally signifies *binding together*. The adjective *constringent* already exists, and is given in all dictionaries.

(b) ON THE EFFECT OF EMPLOYING SOFT PRESSURE-PLATES  
IN EXPERIMENTS ON CRUSHING. (See page 152.)

The cracks observed when soft metal is employed are due to the tearing of the surface by frictional pull, applied by the soft metal as it spreads. This action is familiar to modern experimenters on crushing.

## (c) ON ARSENIC IN GLASS.

Having learned that the oxide of arsenic used in glass-making is always the common white arsenic (arsenious acid,  $\text{As}_2\text{O}_3$ ), whereas the higher oxide (arsenic acid,  $\text{As}_2\text{O}_5$ ) is invariably mentioned in this work, I wrote to Dr. Hovestadt on the subject. The following is a translation of his reply:

"I cannot accept your proposal to print  $\text{As}_2\text{O}_3$  instead of  $\text{As}_2\text{O}_5$ . It is true that the substance put into the mixture is  $\text{As}_2\text{O}_3$ ; but in all the Jena glasses oxidising materials (nitrates) are added—a statement which Dr. Schott has to-day expressly confirmed. These convert the lower oxide into the higher during the melting; and in the glass as finally obtained the  $\text{As}_2\text{O}_5$  is combined with alkali. Dr. Schott adds that, in many commercial glasses, such as plate and sheet glasses,  $\text{As}_2\text{O}_3$  is employed without the addition of oxidising materials, so that no  $\text{As}_2\text{O}_5$  can be formed; but he adds that, in his opinion, no arsenic then remains in the glass; it is driven off in vapour and exercises no influence."

On the other hand, Mr. Walter Rosenhain, of Chance's Glass Works, after considering the above view, writes:

"I have very good ground for believing that, so far as arsenic enters into the composition of glass at all, it is likely to do so as arsenious

acid. The nature of the acids themselves is such as to lead to this belief. Arsenic acid is easily reduced by heat alone, and, though certainly less volatile than  $\text{As}_2\text{O}_3$ , it is still volatile. Further, it is a feeble acid, and at high temperatures, in the presence of such acids as boric or silicic, it would hardly be capable of remaining in combination with alkalies. I believe that arsenic acid or its compounds, when they are present in glass at all, either form insoluble impurities or cause it to become opalescent."

J. D. E.

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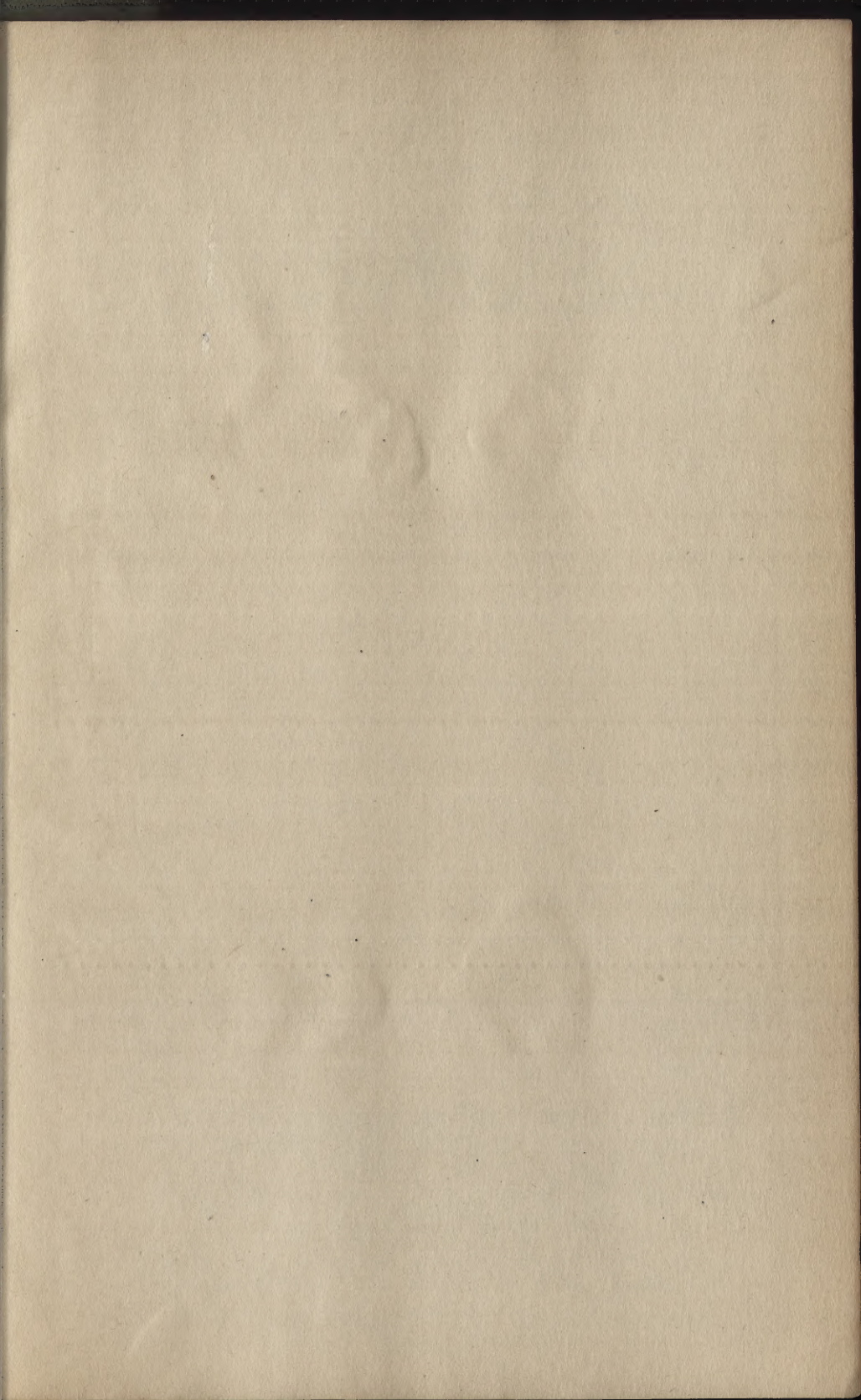
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